

## PATENT COOPERATION TREATY

PCT

NOTIFICATION CONCERNING  
AMENDMENTS OF THE CLAIMS(PCT Rule 62 and  
Administrative Instructions, Section 417)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C. 20231  
ETATS-UNIS D'AMERIQUE

in its capacity as International Preliminary Examining Authority

Date of mailing (day/month/year)

12 October 2000 (12.10.00)

International application No.

PCT/IB00/00234

International filing date (day/month/year)

07 March 2000 (07.03.00)

Applicant

MACKEY, Larry, Neil et al

The International Bureau hereby informs the International Preliminary Examining Authority that no amendments under Article 19 have been received by the International Bureau (Administrative Instructions, Section 417).

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

Olivia TEFY

Telephone No. (41-22) 338.83.38

## PATENT COOPERATION TREATY

PCT

COMMUNICATION OF  
INTERNATIONAL APPLICATIONS

(PCT Article 20)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C. 20231  
ETATS-UNIS D'AMERIQUE

in its capacity as designated Office

Date of mailing:

14 September 2000 (14.09.00)

The International Bureau transmits herewith copies of the international applications having the following international application numbers and international publication numbers:

International application no.:International publication no.:

PCT/IB00/00234

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer:

J. Zahra

Telephone No.: (41-22) 338.83.38

09/914 966

RECORD COPY

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

PCT / IB 0 0 / 0 0 2 3 4	
International Application No.	
07 MARCH 2000	( 0 7. 03. 00 )
International Filing Date	
INTERNATIONAL BUREAU OF WIPO	
PCT International Application	
Name of receiving Office and "PCT International Application"	
Applicant's or agent's file reference (if desired) (12 characters maximum) 7456 R	

Box No. I TITLE OF INVENTION	
ABSORBENT, FLEXIBLE, STRUCTURE COMPRISING STARCH FIBERS	
Box No. II APPLICANT	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	
MACKEY, Larry Neil 5856 Crestview Avenue Fairfield, Ohio 45014 United States of America	
<input checked="" type="checkbox"/> This person is also inventor.	
Telephone No.	
Facsimile No.	
Teleprinter No.	
State (that is, country) of nationality: United States of America	
State (that is, country) of residence: United States of America	
This person is applicant for the purposes of: <input checked="" type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)	
MILLER, II, James Daniel 4108 Benket Drive Cincinnati, Ohio 45241 United States of America	
This person is: <input type="checkbox"/> applicant only <input checked="" type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)	
State (that is, country) of nationality: United States of America	
State (that is, country) of residence: United States of America	
This person is applicant for the purposes of: <input checked="" type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box	
<input checked="" type="checkbox"/> Further applicants and/or (further) inventors are indicated on a continuation sheet.	
Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE	
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: <input checked="" type="checkbox"/> agent <input type="checkbox"/> common representative	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)	
RICHARDS, John Ladas & Parry 26 West 61st Street New York, New York 10023 United States of America	
Telephone No. 212-708-1915	
Facsimile No. 212-2468959	
Teleprinter No.	
<input type="checkbox"/> Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.	

Form PCT/RO/101 (first sheet) (July 1998; reprint July 1999)

See Notes to the request form

Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)	
<i>If none of the following sub-boxes is used, this sheet should not be included in the request.</i>	
<p>Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</p> <p>RICHARDS, Mark Ryan 2912 Elmo Place Middletown, Ohio 45042 United States of America</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)</p>
<p>State (that is, country) of nationality: United States of America</p>	<p>State (that is, country) of residence: United States of America</p>
<p>This person is applicant for the purposes of: <input checked="" type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</p> <p>MICHAEL, John Gerald 2536 Briarcliff Avenue Cincinnati, Ohio 45224 United States of America</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)</p>
<p>State (that is, country) of nationality: United States of America</p>	<p>State (that is, country) of residence: United States of America</p>
<p>This person is applicant for the purposes of: <input checked="" type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</p> <p>CABELL, David William 6646 Powner Farm Drive Cincinnati, Ohio 45248 United States of America</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)</p>
<p>State (that is, country) of nationality: United States of America</p>	<p>State (that is, country) of residence: United States of America</p>
<p>This person is applicant for the purposes of: <input checked="" type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p>Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</p> <p>BAILEY, Valerie Ann 2681 Hilltop Court Florence, Kentucky 41042 United States of America</p>	<p>This person is:</p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)</p>
<p>State (that is, country) of nationality: United States of America</p>	<p>State (that is, country) of residence: United States of America</p>
<p>This person is applicant for the purposes of: <input checked="" type="checkbox"/> all designated States <input type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box</p>	
<p><input type="checkbox"/> Further applicants and/or (further) inventors are indicated on another continuation sheet.</p>	

**Box No.V DESIGNATION OF STATES**

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked):

**Regional Patent**

- ☐ **AP** ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☐ **EA** Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☐ **EP** European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☐ **OA** OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

**National Patent (if other kind of protection or treatment desired, specify on dotted line):**

- |   |   |
|---|---|
| <input type="checkbox"/> AE United Arab Emirates                  | <input type="checkbox"/> LR Liberia                                   |
| <input type="checkbox"/> AL Albania                               | <input type="checkbox"/> LS Lesotho                                   |
| <input type="checkbox"/> AM Armenia                               | <input type="checkbox"/> LT Lithuania                                 |
| <input type="checkbox"/> AT Austria                               | <input type="checkbox"/> LU Luxembourg                                |
| <input type="checkbox"/> AU Australia                             | <input type="checkbox"/> LV Latvia                                    |
| <input type="checkbox"/> AZ Azerbaijan                            | <input type="checkbox"/> MD Republic of Moldova                       |
| <input type="checkbox"/> BA Bosnia and Herzegovina                | <input type="checkbox"/> MG Madagascar                                |
| <input type="checkbox"/> BB Barbados                              | <input type="checkbox"/> MK The former Yugoslav Republic of Macedonia |
| <input type="checkbox"/> BG Bulgaria                              |   |
| <input type="checkbox"/> BR Brazil                                | <input type="checkbox"/> MN Mongolia                                  |
| <input type="checkbox"/> BY Belarus                               | <input type="checkbox"/> MW Malawi                                    |
| <input type="checkbox"/> CA Canada                                | <input type="checkbox"/> MX Mexico                                    |
| <input type="checkbox"/> CH and LI Switzerland and Liechtenstein  | <input type="checkbox"/> NO Norway                                    |
| <input type="checkbox"/> CN China                                 | <input type="checkbox"/> NZ New Zealand                               |
| <input type="checkbox"/> CU Cuba                                  | <input type="checkbox"/> PL Poland                                    |
| <input type="checkbox"/> CZ Czech Republic                        | <input type="checkbox"/> PT Portugal                                  |
| <input type="checkbox"/> DE Germany                               | <input type="checkbox"/> RO Romania                                   |
| <input type="checkbox"/> DK Denmark                               | <input type="checkbox"/> RU Russian Federation                        |
| <input type="checkbox"/> EE Estonia                               | <input type="checkbox"/> SD Sudan                                     |
| <input type="checkbox"/> ES Spain                                 | <input type="checkbox"/> SE Sweden                                    |
| <input type="checkbox"/> FI Finland                               | <input type="checkbox"/> SG Singapore                                 |
| <input type="checkbox"/> GB United Kingdom                        | <input type="checkbox"/> SI Slovenia                                  |
| <input type="checkbox"/> GD Grenada                               | <input type="checkbox"/> SK Slovakia                                  |
| <input type="checkbox"/> GE Georgia                               | <input type="checkbox"/> SL Sierra Leone                              |
| <input type="checkbox"/> GH Ghana                                 | <input type="checkbox"/> TJ Tajikistan                                |
| <input type="checkbox"/> GM Gambia                                | <input type="checkbox"/> TM Turkmenistan                              |
| <input type="checkbox"/> HR Croatia                               | <input type="checkbox"/> TR Turkey                                    |
| <input type="checkbox"/> HU Hungary                               | <input type="checkbox"/> TT Trinidad and Tobago                       |
| <input type="checkbox"/> ID Indonesia                             | <input type="checkbox"/> UA Ukraine                                   |
| <input type="checkbox"/> IL Israel                                | <input type="checkbox"/> UG Uganda                                    |
| <input type="checkbox"/> IN India                                 | <input checked="" type="checkbox"/> US United States of America       |
| <input type="checkbox"/> IS Iceland                               |   |
| <input type="checkbox"/> JP Japan                                 |   |
| <input type="checkbox"/> KE Kenya                                 |   |
| <input type="checkbox"/> KG Kyrgyzstan                            |   |
| <input type="checkbox"/> KP Democratic People's Republic of Korea |   |
|   |   |
| <input type="checkbox"/> KR Republic of Korea                     |   |
| <input type="checkbox"/> KZ Kazakhstan                            |   |
| <input type="checkbox"/> LC Saint Lucia                           |   |
| <input type="checkbox"/> LK Sri Lanka                             |   |

Continuation in Part

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

**Precautionary Designation Statement:** In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)

**Supplemental Box** *If the Supplemental Box is not used, this sheet should not be included in the request.*

1. If, in any of the Boxes, the space is insufficient to furnish all the information: in such case, write "Continuation of Box No. ..." (indicate the number of the Box) and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:

- (i) If more than two persons are involved as applicants and/or inventors and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
- (ii) if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "the States indicated in the Supplemental Box" is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
- (iii) if, in Box No. II or in any of the sub-boxes of Box No. III, the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
- (iv) if, in addition to the agent(s) indicated in Box No. IV, there are further agents: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;
- (v) if, in Box No. V, the name of any State (or OAPI) is accompanied by the indication "patent of addition," or "certificate of addition," or if, in Box No. V, the name of the United States of America is accompanied by an indication "continuation" or "continuation-in-part": in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
- (vi) if, in Box No. VI, there are more than three earlier applications whose priority is claimed: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI;
- (vii) if, in Box No. VI, the earlier application is an ARIPO application: in such case, write "Continuation of Box No. VI", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed.

2. If, with regard to the precautionary designation statement contained in Box No. V, the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded.

3. If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning non-prejudicial disclosures or exceptions to lack of novelty: in such case, write "Statement concerning non-prejudicial disclosures or exceptions to lack of novelty" and furnish that statement below.

**CONTINUATION OF BOX NO. IV**

HANDELMAN, Joseph H.  
GALLOWAY, Peter D.  
CORD, Janet I.

Telephone No. 212-708-1880  
Telephone No. 212-708-1905  
Telephone No. 212-708-1935

LADAS & PARRY  
26 West 61st Street  
New York, New York 10023  
United States of America

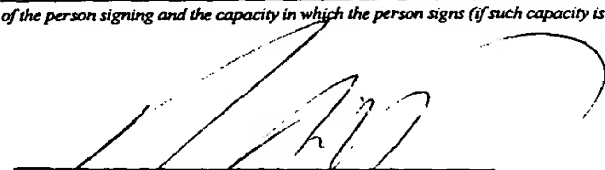
BAILLIE, Iain C.  
MOLYNEAUX, Martyn W.  
EBNER VON ESCHENBACH, Jennifer

Telephone No. 089 26 90 77  
Telephone No. 089 26 90 77  
Telephone No. 089 26 90 77

LADAS & PARRY  
Dachauerstrasse 37  
80335 Munich  
Germany

**CONTINUATION OF BOX NO. V**

United States of America Application No. 09/264,401  
Filed 08 March 1999 (08.03.99)

<b>Box No. VI PRIORITY CLAIM</b>		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application:* regional Office	international application: receiving Office
item (1) 08 March 1999 (08.03.99)	09/264,401	US		
item (2)				
item (3)				
<input type="checkbox"/> The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s):				
* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.				
<b>Box No. VII INTERNATIONAL SEARCHING AUTHORITY</b>				
Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):		Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):		
ISA/US		Date (day/month/year)      Number      Country (or regional Office) 08 March 1999      09/264,401      US (08.03.99)		
<b>Box No. VIII CHECK LIST; LANGUAGE OF FILING</b>				
This international application contains the following number of sheets: request : 5 description (excluding sequence listing part) : 54 claims : 1 abstract : 1 drawings : 7 sequence listing part of description : Total number of sheets : 68		This international application is accompanied by the item(s) marked below: 1. <input checked="" type="checkbox"/> fee calculation sheet 2. <input type="checkbox"/> separate signed power of attorney 3. <input type="checkbox"/> copy of general power of attorney; reference number, if any: 4. <input type="checkbox"/> statement explaining lack of signature 5. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s): 6. <input type="checkbox"/> translation of international application into (language): 7. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material 8. <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form 9. <input checked="" type="checkbox"/> other (specify): Additional Page		
Figure of the drawings which should accompany the abstract:		Language of filing of the international application: English		
<b>Box No. IX SIGNATURE OF APPLICANT OR AGENT</b>				
Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).				
 JOHN RICHARDS AGENT FOR APPLICANTS				

For receiving Office use only		2. Drawings:  <input type="checkbox"/> received:  <input type="checkbox"/> not received:
1. Date of actual receipt of the purported international application:	07 MARCH 2000 (07.03.00)	
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:		
4. Date of timely receipt of the required corrections under PCT Article 11(2):		
5. International Searching Authority (if two or more are competent): ISA/US	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.	

For International Bureau use only	
Date of receipt of the record copy by the International Bureau:	10 MARCH 2000 (10.03.00)

# PATENT COOPERATION TREATY

PCT/IB00/00234  
U 013595-2

## PCT

### NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

From the INTERNATIONAL BUREAU


To:

RICHARDS, John  
Ladas & Parry  
26 West 61st Street  
New York, NY 10023  
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 16 May 2000 (16.05.00)	
Applicant's or agent's file reference 7456 R	<b>IMPORTANT NOTIFICATION</b>
International application No. PCT/IB00/00234	International filing date (day/month/year) 07 March 2000 (07.03.00)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 08 March 1999 (08.03.99)
Applicant MACKEY, Larry, Neil et al	

1. The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
2. This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
3. An asterisk(\*) appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, **the attention of the applicant is directed to Rule 17.1(c)** which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
4. The letters "NR" appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, **the attention of the applicant is directed to Rule 17.1(c)** which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
08 Marc 1999 (08.03.99)	09/264,401	US	10 May 2000 (10.05.00)

<p style="text-align: center;">The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No. (41-22) 740.14.35</p>	<p>Authorized officer</p> <p style="text-align: right;">Lazar  Panakal</p> <p>Telephone No. (41-22) 338.83.38</p>
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PCT

NOTICE INFORMING THE APPLICANT OF THE  
COMMUNICATION OF THE INTERNATIONAL  
APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

From the INTERNATIONAL BUREAU

To:

RICHARDS, John  
Ladas & Parry  
26 West 61st Street  
New York, NY 10023  
ETATS-UNIS D'AMERIQUE

Date of mailing (day/month/year) 14 September 2000 (14.09.00)		IMPORTANT NOTICE	
Applicant's or agent's file reference 7456 R			
International application No. PCT/IB00/00234	International filing date (day/month/year) 07 March 2000 (07.03.00)	Priority date (day/month/year) 08 March 1999 (08.03.99)	
Applicant MACKEY, Larry, Neil et al			

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:  
US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:  
None

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

**REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)**

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a demand for international preliminary examination must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

**REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))**

If the applicant wishes to proceed with the international application in the national phase, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. (41-22) 740.14.35	Authorized officer J. Zahra Telephone No. (41-22) 338.83.38
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From the INTERNATIONAL SEARCHING AUTHORITY

To: JOHN RICHARDS  
LADAS & PERRY  
26 WEST 61ST STREET  
NEW YORK, NEW YORK 10023

**PCT**

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL SEARCH REPORT  
OR THE DECLARATION

(PCT Rule 44.1)

Date of Mailing  
(day/month/year)

**21 JUN 2000**

Applicant's or agent's file reference

7456 R

**FOR FURTHER ACTION** See paragraphs 1 and 4 below

International application No.

PCT/IB00/00234

International filing date  
(day/month/year)

07 MARCH 2000

Applicant

MACKEY, LARRY NEIL

1. ☒ The applicant is hereby notified that the international search report has been established and is transmitted herewith.

**Filing of amendments and statement under Article 19:**

The applicant is entitled, if he so wishes, to amend the claims of the international application (see Rule 46):

**When?** The time limit for filing such amendments is normally 2 months from the date of transmittal of the international search report; however, for more details, see the notes on the accompanying sheet.

**Where?** Directly to the International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland  
Facsimile No.: (41-22) 740.14.35

**For more detailed instructions,** see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no international search report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in rules 90 *bis* 1 and 90 *bis* 3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the ISA/US

Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JOHN J. GUARRIELLO

Telephone No. (703) 308-0651

## PATENT COOPERATION TREATY

U 013595-2

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: JOHN RICHARDS  
LADAS & PERRY  
26 WEST 61ST STREET  
NEW YORK, NEW YORK 10023

**PCT**NOTIFICATION OF TRANSMITTAL OF  
INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT

(PCT Rule 71.1)

Date of Mailing  
(day/month/year)

29 MAY 2001

Applicant's or agent's file reference  
7456 R

## IMPORTANT NOTIFICATION

International application No.

PCT/IB00/00234

International filing date (day/month/year)

07 MARCH 2000

Priority Date (day/month/year)

08 MARCH 1999

Applicant

MACKEY, LARRY NEIL

JUN 4 2001

I P-N.Y.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JOHN J. GUARRIELLO

Telephone No. (703) 308-0651

Form PCT/IPEA/416 (July 1992) ★

EL728214946US

ENTRY 15 TERM

JR 49769 6/29/01

## PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 7456 R	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/IB00/00234	International filing date (day/month/year) 07 MARCH 2000	Priority date (day/month/year) 08 MARCH 1999
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.		
Applicant MACKEY, LARRY NEIL		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets.
- ☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).
- These annexes consist of a total of 0 sheets.

## 3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 02 AUGUST 2000	Date of completion of this report 04 MAY 2001
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer JOHN J. GUARRIELLO <i>John J. Guarriello</i>
Facsimile No. (703) 305-3230	Telephone No. (703) 308-0651

Form PCT/IPEA/409 (cover sheet) (July 1998) ★

EL728214946US

**I. Basis of the report****1. With regard to the elements of the international application:\***☒ the international application as originally filed☒ the description:

pages 1-57 , as originally filed  
pages NONE , filed with the demand  
pages NONE , filed with the letter of \_\_\_\_\_

☒ the claims:

pages 58-59 , as originally filed  
pages NONE , as amended (together with any statement) under Article 19  
pages NONE , filed with the demand  
pages NONE , filed with the letter of \_\_\_\_\_

☒ the drawings:

pages 1-7 , as originally filed  
pages NONE , filed with the demand  
pages NONE , filed with the letter of \_\_\_\_\_

☒ the sequence listing part of the description:

pages NONE , as originally filed  
pages NONE , filed with the demand  
pages NONE , filed with the letter of \_\_\_\_\_

**2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.**

These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

**3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:**

- ☐ contained in the international application in printed form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

**4. ☒ The amendments have resulted in the cancellation of:**

☒ the description, pages NONE  
☒ the claims, Nos. NONE  
☒ the drawings, sheets/fig NONE

**5. ☐ This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\***

*\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

*\*\*Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/IB00/00234

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. statement**

Novelty (N)	Claims <u>2-10</u>	YES
	Claims <u>1</u>	NO
Inventive Step (IS)	Claims <u>NONE</u>	YES
	Claims <u>1-10</u>	NO
Industrial Applicability (IA)	Claims <u>1-10</u>	YES
	Claims <u>NONE</u>	NO

**2. citations and explanations (Rule 70.7)**

Claim 1 lacks novelty under PCT Article 33(2) as being anticipated by BRUNN 2,570,449.

BRUNN describes a pseudo-thermoplastic starch which is made by adding solvents, softeners, or fluxes to produce softening or liquefying properties, (column 1, lines 31-52). BRUNN describes the production of starch into fibers and other items, (column 2, lines 49-55). BRUNN describes the essential limitations of the claim. Claim lacks novelty.

Claims 2-10 lack an inventive step under PCT Article 33(3) as being obvious over BRUNN 2,750,449 in view of BUEHLER ET AL. 5,516,815.

BRUNN describes pseudo-thermoplastic starch fibers, which is made by adding solvents, softeners, or fluxes to produce softening or liquefying properties, (column 1, lines 31-52). BRUNN describes the production of this starch into fibers and other items, (column 2, lines 49-55). BRUNN describes the production of this starch, pseudo-thermoplastic, into articles which can be regenerated for other uses and other materials, (column 3, lines 36-69). Brunn differs from the claimed invention because the specific plasticizers and crosslinking agents are not stated.

BUEHLER describes starch containing fibers and the modification of the starch fibers, which the examiner is understanding to be pseudo-thermoplastic starch, (see abstract, column 1, lines 17-65). BUEHLER describes this starch in a matrix material, (column 2, lines 10-66). BUEHLER describes additives, (column 4, lines 5-67), plasticizers, and crosslinking agents that can be used, (column 5, lines 1-49).

It would have been obvious to one of ordinary skill in the art to modify BRUNN because BUEHLER describes the specific plasticizers and crosslinking agents which BRUNN describes as additives and the expectation would be enhanced properties of biodegradability. Moreover, BUEHLER describes adding 0-20 parts of the materials, which overlaps the amounts of the components of the claimed invention. It would be obvious to the skilled artisan to optimize these amounts since BRUNN and BUEHLER describe the claimed (Continued on Supplemental Sheet.)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/IB00/00234

**Supplemental Box**

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

**CLASSIFICATION:**

The International Patent Classification (IPC) and/or the National classification are as listed below:

IPC(7): C08L 3/00, 77/02; D02G 3/00. and US Cl.: 428/364, 913; 442/414; 106/206.1; 523/124, 128; 524/47.

V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):  
components.

Claims 1-10 meet the criteria set out in PCT Article 33(4), because the the pseduo-thermoplastic starch fibers with low density represent an improvement in biodegradabiltiy.

----- NEW CITATIONS -----

NONE

## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 7456 R	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/IB00/00234	International filing date ( <i>day/month/year</i> ) 07 MARCH 2000	(Earliest) Priority Date ( <i>day/month/year</i> ) 08 MARCH 1999
Applicant MACKEY, LARRY NEIL		

This international search report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This international search report consists of a total of 2 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

## 1. Basis of the report

a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing:

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

2. ☐ Certain claims were found unsearchable (See Box I).

3. ☐ Unity of invention is lacking (See Box II).

4. With regard to the title,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No. \_\_\_\_\_

☐ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

☐ None of the figures.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB00/00234

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : C08L 3/00, 77/02; D02G 3/00.

US CL : 428/364, 913; 442/414; 106/206.1; 523/124, 128; 524/47.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/364, 913; 442/414; 106/206.1; 523/124, 128; 524/47.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2,570,449 A (BRUNN) 09 October 1951, col. 1, lines 32-51; col. 2, lines 49-52.	1
Y	US 5,516,815 A (BUEHLER et al.) 14 May 1996, see whole document.	1-10
Y	US 5,346,936 A (BUEHLER et al.) 13 September 1994, see whole document.	1-10
Y	US 5,444,113 A (SINCLAIR et al) 22 August 1995, see whole document.	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

25 MAY 2000

Date of mailing of the international search report

21 JUN 2000

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JOHN J. GUARRIELLO

Telephone No. (703) 308-0651

## PATENT COOPERATION TREATY

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITYTo: JOHN RICHARDS  
LADAS & PERRY  
26 WEST 61ST STREET  
NEW YORK, NEW YORK 10023

PCT

WRITTEN OPINION

(PCT Rule 66)

Date of Mailing  
(day/month/year)

22 DEC 2000

Applicant's or agent's file reference

7456 R

REPLY DUE

within TWO months  
from the above date of mailing

International application No.

PCT/IB00/00234

International filing date (day/month/year)

07 MARCH 2000

Priority date (day/month/year)

08 MARCH 1999

International Patent Classification (IPC) or both national classification and IPC  
Please See Supplemental Sheet.

Applicant

MACKEY, LARRY NEIL

1. This written opinion is the first (first, etc.) drawn by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

When? See the time limit indicated above. ~~The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).~~

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also For an additional opportunity to submit amendments, see Rule 66.4.  
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 *bis*.  
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 08 JULY 2001Name and mailing address of the IPEA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JOHN J. GUARRIELLO

Telephone No. (703) 308-0651

WRITTEN OPINION

International application No.

PCT/IB00/00234

1. Basis of the opinion

1. With regard to the elements of the international application: \*

☒ the international application as originally filed

☒ the description:

pages 1-54 , as originally filed  
pages NONE , filed with the demand  
pages NONE , filed with the letter of

☒ the claims:

pages 55 , as originally filed  
pages NONE , as amended (together with any statement) under Article 19  
pages NONE , filed with the demand  
pages NONE , filed with the letter of

☒ the drawings:

pages 1-7 , as originally filed  
pages NONE , filed with the demand  
pages NONE , filed with the letter of

☒ the sequence listing part of the description:

pages NONE , as originally filed  
pages NONE , filed with the demand  
pages NONE , filed with the letter of

2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language \_\_\_\_\_ which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).  
☐ the language of publication of the international application (under Rule 48.3(b)).  
☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the written opinion was drawn on the basis of the sequence listing:

- ☐ contained in the international application in printed form.  
☐ filed together with the international application in computer readable form.  
☐ furnished subsequently to this Authority in written form.  
☐ furnished subsequently to this Authority in computer readable form.  
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.  
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. ☒ The amendments have resulted in the cancellation of:

☒ the description, pages NONE  
☒ the claims, Nos. NONE  
☒ the drawings, sheets/fig. NONE

5. ☐ This opinion has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".

## WRITTEN OPINION

International application No.

PCT/IB00/00234

**V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. statement**

Novelty (N)	Claims <u>2-10</u>	YES
	Claims <u>1</u>	NO
Inventive Step (IS)	Claims <u>NONE</u>	YES
	Claims <u>1-10</u>	NO
Industrial Applicability (IA)	Claims <u>1-10</u>	YES
	Claims <u>NONE</u>	NO

**2. citations and explanations**

Claim 1 lacks novelty under PCT Article 33(2) as being anticipated by BRUNN 2,570,449.

BRUNN describes a pseudo-thermoplastic starch which is made by adding solvents, softeners, or fluxes to produce softening or liquefying properties, (column 1, lines 31-52). BRUNN describes the production of starch into fibers and other items, (column 2, lines 49-55). BRUNN describes the essential limitations of the claim. Claim lacks novelty.

Claims 2-10 lack an inventive step under PCT Article 33(3) as being obvious over BRUNN 2,750,449 in view of BUEHLER ET AL. 5,516,815.

BRUNN describes pseudo-thermoplastic starch fibers, which is made by adding solvents, softeners, or fluxes to produce softening or liquefying properties, (column 1, lines 31-52). BRUNN describes the production of this starch into fibers and other items, (column 2, lines 49-55). BRUNN describes the production of this starch, pseudo-thermoplastic, into articles which can be regenerated for other uses and other materials, (column 3, lines 36-69). Brunn differs from the claimed invention because the specific plasticizers and crosslinking agents are not stated.

BUEHLER describes starch containing fibers and the modification of the starch fibers, which the examiner is understanding to be pseudo-thermoplastic starch, (see abstract, column 1, lines 17-65). BUEHLER describes this starch in a matrix material, (column 2, lines 10-66). BUEHLER describes additives, (column 4, lines 5-67), plasticizers, and crosslinking agents that can be used, (column 5, lines 1-49).

It would have been obvious to one of ordinary skill in the art to modify BRUNN because BUEHLER describes the specific plasticizers and crosslinking agents which BRUNN describes as additives and the expectation would be enhanced properties of biodegradability. Moreover, BUEHLER describes adding 0-20 parts of the materials, which overlaps the amounts of the components of the claimed invention. It would be obvious to the skilled artisan to optimize these amounts since BRUNN and BUEHLER describe the claimed (Continued on Supplemental Sheet.)

WRITTEN OPINION

International application No.

PCT/IB00/00234

**Supplemental Box**

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

**TIME LIMIT:**

The time limit set for response to a Written Opinion may not be extended. 37 CFR 1.484(d). Any response received after the expiration of the time limit set in the Written Opinion will not be considered in preparing the International Preliminary Examination Report.

**CLASSIFICATION:**

The International Patent Classification (IPC) and/or the National classification are as listed below:  
IPC(7): C08L 3/00, 77/02; D02G 3/00. and US Cl.: 428/364, 913; 442/414; 106/206.1; 523/124, 128; 524/47.

**V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):**  
components.

Claims 1-10 meet the criteria set out in PCT Article 33(4), because the the pseduo-thermoplastic starch fibers with low density represent an improvement in biodegradability.

----- NEW CITATIONS -----

NONE

09/914966013595-2  
518 Rec'd PCT/PTO 0.6 SEP 2001

7/ppts

- 1 -

ABSORBENT, FLEXIBLE, STRUCTURE COMPRISING STARCH FIBERSFIELD OF THE INVENTION

The present invention relates to pseudo-thermoplastic starch extruded in the form of fibers. Starch may be extruded and either meltblown or spunbonded to form fibrous low density structures.

BACKGROUND OF THE INVENTION

It is well recognized that starch molecules come in two forms: the substantially linear amylose polymer and the highly branched amylopectin polymer. These two forms of starch have very different properties, probably due to the ease of association of the hydroxyl groups among different molecules. The molecular structure of amylose is essentially linear with two to five relatively long branches. The average degree of polymerization of the branches is about 350 monomer units. Under conditions that provide sufficient freedom of molecular movements, primarily by dilution with suitable solvents, and in some instances, dilution coupled with heating, the linear amylose chains can be oriented into preferentially parallel alignments such that the hydroxyl groups on one chain are in close proximity with those on the adjacent chains. The alignment of neighboring amylose molecules is believed to facilitate intermolecular hydrogen bonding. Consequently the amylose molecules form strong aggregates. In contrast, the molecular structure of amylopectin is highly branched via 1,6- $\alpha$  linkages. The average degree of polymerization of the branches is about 25 monomer units. Due to the highly branched structure, the amylopectin molecules can not move as freely and do not align and associate as readily.

Attempts have been made to process natural starch on standard equipment and existing technology known in the plastic industry. Since natural starch generally has a granular structure, it needs to be "destructurized" and/or modified before it can be melt processed like a thermoplastic material. For destructurization, the starch is typically heated above its softening and melting temperature under a pressurized condition. Melting and disordering of the molecular structure of the starch granule takes place and a destructurized starch is obtained. Chemical or enzymatic agents may also be used to destructurize, oxidize, or derivatize the starch. Modified starches have been used to make biodegradable plastics, wherein the modified starch is

- 2 -

blended as an additive or the minor component with petroleum-based or synthetic polymers. However, when the modified starch is processed by itself or as the major component in a blend with other materials using conventional thermoplastic processing techniques, such as molding or extrusion, the finished parts tend to have a high incidence of defects. Moreover, the modified starch (alone or as the major component of a blend) has been found to have poor melt extensibility; consequently, it cannot be successfully processed by uniaxial or biaxial extensional processes into fibers, films, foams or the like.

Previous attempts to produce starch fibers relate principally to wet-spinning processes. For Example, a starch/solvent colloidal suspension can be extruded from a spinneret into a coagulating bath. This process relies on the marked tendency of amylose to align and form strongly associated aggregates to provide strength and integrity to the final fiber. Any amylopectin present is tolerated as an impurity that adversely affects the fiber spinning process and the strength of the final product. Since it is well known that natural starch is rich in amylopectin, earlier approaches include pre-treating the natural starch to obtain the amylose-rich portion desirable for fiber spinning. Clearly this approach is not economically feasible on a commercial scale since a large portion (i.e, the amylopectin portion) of the starch is discarded. In more recent developments, natural starch, typically high in natural amylopectin content, can be wet-spun into fibers. However, the wet-spun fibers are coarse, typically having fiber diameters greater than 50 microns. Additionally, the large quantity of solvent used in this process requires an additional drying step and a recovery or treatment step of the effluent. Some references for wet-spinning starch fibers include U.S. Patent No. 4,139,699 issued to Hernandez et al. on February 13, 1979; U.S. Patent No. 4,853,168 issued to Eden et al. on August 1, 1989; and U.S. Patent No. 4,234,480 issued to Hernandez et al. on January 6, 1981.

U.S. Patent Nos. 5,516,815 and 5,316,578 to Buehler et al. relate to starch compositions for making starch fibers from a melt spinning process. The melt starch composition is extruded through a spinnerette to produce filaments having diameters slightly enlarged relative to the diameter of the die orifices on the spinnerette (i.e., a die swell effect). The filaments are subsequently drawn down mechanically or

thermomechanically by a drawing unit to reduce the fiber diameter. The major disadvantage of the starch composition of Buehler et al. is that it does not use high molecular weight polymers, which enhance the melt extensibility of starch compositions. Consequently, the starch composition of Buehler et al. could not be  
5 successfully melt attenuated to produce fine fibers of 25 microns or less in diameter.

Other thermoplastically processable starch compositions are disclosed in U.S. Patent No. 4,900,361, issued on August 8, 1989 to Sachetto et al.; U.S. Patent No. 5,095,054, issued on March 10, 1992 to Lay et al.; U.S. Patent No. 5,736,586, issued on April 7, 1998 to Bastioli et al.; and PCT publication WO 98/40434 filed by  
10 Hanna et al. published March 14, 1997. These starch compositions do not contain the high molecular weight polymers that are necessary to achieve the desired melt viscosity and melt extensibility, which are critical material characteristics to producing fine fibers, thin films or thin-walled foams.

Cellulose fibrous webs such as paper are well known in the art. Low  
15 density fibrous webs are in common use today in products such as paper towels, toilet tissue, facial tissue, napkins, wet wipes, and the like. The large demand for such paper products has created a need for improvements in the products and in the methods of their manufacture.

There are several well known concerns regarding the papermaking  
20 industry requiring papermaking manufacturers to balance the costs of machinery and resources with the total cost of delivering the paper products to the consumers. First instance, the popularity of paper products has created an increasing demand on wood based cellulosic fibers resulting in a rapid depletion of trees due to deforestation.

In addition, during conventional papermaking operations wood  
25 cellulosic fibers are repulped, beaten or refined to achieve a level of fiber hydration in order to form an aqueous pulp slurry. Processes for the making of paper products for use in tissue, toweling, and sanitary products generally involve the preparation of the aqueous slurry and then subsequently removing the water from the slurry while contemporaneously rearranging the fibers therein to form a paper web. Subsequent to  
30 dewatering, the web is processed into a dry roll or sheet form and eventually converted into a consumer package. Various types of machinery must be employed to assist in



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the dewatering process and converting operations requiring a significant investment in capital.

Further, the conventional papermaking operation involves the incorporation of additives into the pulp in order to achieve specific end properties. For instance, additives such as strength resins, debonding surfactants, softening agents, pigments, lattices, synthetic microspheres, fire-retardants, dyes, perfumes, etc., are often employed in the manufacture of paper. The efficient retention of these additives at the wet end of a papermaking process presents difficulty to the manufacturer since that portion which is not retained creates not only an economic loss but also significant pollution problems if it becomes part of a plant effluent. Additives can also be added to the paper web subsequent to dewatering via coating or saturation processes commonly known in the art. These processes usually require that excess heating energy be consumed to redry the paper after coating. Moreover, in some instances, the coating systems are required to be solvent based which increases capital costs and requires recovery of volatile materials to meet regulatory requirements.

Various natural fibers other than cellulose as well as a variety of synthetic fibers have been employed in making paper. However, these replacements have failed to provide a commercially acceptable substitute for cellulose due to their high cost, poor bonding properties, chemical incompatibilities, and handling difficulties in papermaking systems. Starch fibers have been suggested as a substitute for cellulose in various aspects of the papermaking process, however, commercial attempts to use such fibers have been unsuccessful. As a result, paper products are still being manufactured almost exclusively from wood base cellulosic ingredients.

Starch is a plant carbohydrate having a structure analogous to cellulose. Whereas cellulose is a polymer of D-glucan monomers connected via 1,4- $\beta$  linkages, starch is a polymer of D-glucose monomers connected via primarily 1,4- $\alpha$  linkages. Because starch is available via agricultural resources, it is cheap and plentiful. While starch has been incorporated into various aspects of the papermaking process, attempts to use starch fibers as cellulose fiber replacement in commercial papermaking processes have not been successful.

Consequently, there is a need for an inexpensive and melt processable

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composition from natural starches. Such a melt processable starch composition should not require evaporation of a large quantity of solvents or produce a large amount of effluent during the processing operation. Moreover, such a starch composition should have melt rheological properties suitable for use in conventional plastic processing equipment

There is also a need for a starch composition suitable for use in uniaxial or biaxial extensional processes to produce fibers, films, sheets, foams, shaped articles, and the like economically and efficiently. Specifically, the starch composition should have melt rheological properties suitable for uniaxially or biaxially extensional processes in its melt phase in a substantially continuous manner, i.e., without excessive amount of melt fracture or other defects.

Further, there is a need for a low density flexible structure comprising starch fibers utilizing extrusion and fiber spinning techniques. Particularly, a low density flexible structure comprising starch fibers, wherein the structure has improved tensile strength, softness, and absorbency properties relative to cellulosic pulp fiber structures and the like, while maintaining biodegradability and flushability.

#### SUMMARY OF THE INVENTION

The present invention provides an absorbent flexible structure comprising starch fibers. Naturally occurring starch in the presence of water, plasticizers and other additives is melt extruded and spun into fibers to form an absorbent flexible structure having an apparent density ranging from 0.02 g/cm<sup>3</sup> to 0.20 g/cm<sup>3</sup> and a basis weight ranging from 10 g/m<sup>2</sup> to 450 g/m<sup>2</sup>.

The starch fibers making up the structure can have a size ranging from about 0.01 decitex to about 135 decitex. In a preferred embodiment the fibers can have a size ranging from about 0.02 decitex to about 30 decitex, and most preferably ranging from about 0.02 to about 5 decitex. In addition, fibers making up the structure of the present invention can have a glass transition temperature ranging from about -30 °C to about 150 °C, more preferably from about -30 °C to about 100 °C, and most preferably from about -30 °C to about 25 °C.

Exemplary physical properties of the flexible structure of the present invention include dry tensile strength and wet tensile strength. The dry tensile strength

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of the structure, which is measured as a geometric mean tensile strength, can range from about 10 g/cm to about 1200 g/cm, more preferably from about 30 g/cm to about 600 g/cm, and most preferably from about 40 g/cm to about 475 g/cm. The wet tensile strength of the structure, which is also measured as a geometric mean tensile strength, can range from about 2 g/cm to about 400 g/cm, and more preferably from about 2 g/cm to about 200 g/cm.

#### BRIEF DESCRIPTION OF THE DRAWINGS

These and other features, aspects and advantages of the present invention will become better understood with regard to the following description, appended claims, and accompanying drawings where:

Figure 1a illustrates a torque rheometer assembly used to produce starch fibers.

Figure 1b illustrates the twin screw elements attached to the drive unit and disposed within the barrel of the torque rheometer assembly illustrated in Figure 1a.

Figure 1c shows a torque rheometer assembly having a melt blowing die used to produce fine starch fibers of the present invention.

Figure 2a illustrates a vented twin screw extruder assembly.

Figure 2b illustrates the screw and mixing element configuration for the extrusion assembly depicted in Figure 2a.

Figure 3a illustrates a non-vented twin screw extruder assembly.

Figure 3b illustrates the screw and mixing element configuration for the extrusion assembly depicted in Figure 3a.

Figure 4 illustrates a spinneret and a drawing unit used for pseudo-thermoplastic starch melt fiber spinning.

Figure 5 illustrates the sample rack and cover used for determining absorbency of the starch fiber structures.

Figure 6 illustrates the cross section of the frames for the sample rack and cover illustrated in Figure 5.

Figure 7a is the Scanning Electron Micrographs of fine starch fibers of the present invention shown on a 200 micron scale.

Figure 7b is the Scanning Electron Micrographs of fine starch fibers of the present invention shown on a 20 micron scale.

### DETAILED DESCRIPTION OF THE INVENTION

#### Definitions

5 As used herein, the following terms have the following meanings:

Pseudo-thermoplastic composition is intended to denote materials which by the influence of elevated temperatures may be softened to such a degree that they can be brought into a flowable state, and in this condition may be shaped as desired. Pseudo-thermoplastic materials may be formed under simultaneous influence  
10 of heat and pressure. Pseudo-thermoplastic compositions differ from thermoplastic compositions in that the softening or liquefying of the pseudo-thermoplastic is caused by softeners or solvents present without which it would be impossible to bring them by any temperature or pressure into a soft or flowable condition necessary for shaping since pseudo thermoplastics do not melt as such. The influence of water content on  
15 the glass transition temperature and melting temperature of starch can be measured by differential scanning calorimetry as described by Zeleznak and Hoseny, "Cereal Chemistry", Vol. 64, No. 2, pp. 121-124, 1987.

Pseudo-thermoplastic melt is a pseudo-thermoplastic material in a flowable state.

20 Glass transition temperature,  $T_g$ , is the temperature at which the material changes from a viscous or rubbery condition to a hard and relatively brittle condition.

Basis weight is the weight (in grams) per unit area (in square meters) of a sample reported in grams per square meter.

25 Caliper is the macroscopic thickness of a sample measured as described below.

Apparent density is the basis weight of the sample divided by the caliper with appropriate unit conversions incorporated therein. Apparent density used herein has the units of grams / centimeters cubed ( $\text{g/cm}^3$ ).

30 Machine direction, designated MD, is the direction parallel to the flow of the starch fiber structure through the product manufacturing equipment.

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Cross machine direction, designated CD, is the direction perpendicular to the machine direction in the same plane of the starch fiber structure.

Geometric Mean Dry Tensile Strength (GMDT) is the square root of the product of the machine and cross-machine dry tensile strengths (in grams/cm). The value of GMDT is reported in grams/cm.

Geometric mean wet tensile strength (GMWT) is the square root of the product of the machine and cross-machine wet tensile strengths (in grams/cm). The value of GMWT is reported in grams/cm.

Structure is an arrangement of one or more parts forming a substance or body.

Absorbency is the ability of a material to take up fluids by various means including capillary, osmotic, solvent or chemical action and retain such fluids.

Flexibility indicates the capability of being deformed under a given load without being broken and with or without returning of itself to its former shape.

A fiber is a slender object having a major axis which is very long compared to the two orthogonal axes and having an aspect ratio of at least 4/1, preferably at least 10/1.

Decitex, dtex, is a unit of measure for a fiber expressed in  $\frac{\text{grams}}{10,000 \text{ meters}}$

Flushability is determined by the geometric mean decayed wet tensile strength (GMDWT) (defined below). A flushable structure has a geometric mean decayed wet tensile of less than about 20 g/cm and more preferably less than about 10 g/cm.

The term "bound water" means the water found naturally occurring in starch and before mixing of starch with other components to make the composition of the present invention. The term "free water" means the water that is added in making the composition of the present invention. A person of ordinary skill in the art would recognize that once the components are mixed in a composition, water can no longer be distinguished by its origin.

All percentages, ratios and proportions used herein are by weight

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percent of the composition, unless otherwise specified.

The specification contains a detailed description of (1) exemplary materials of the present invention, (2) exemplary processes for producing the present invention, (3) material properties of the present invention, and (4) analytical procedures for measuring properties of the present invention

(1) Exemplary Materials

For the present invention a starch polymer is mixed with water, plasticizers and other additives and melt extruded to produce fibers. Standard meltblowing or spunbonding techniques are used to produce starch fiber structures.

Such structures may be absorbent and flexible. These structures may be used as substitutes for paper products such as paper towels, napkins, toilet tissues, facial tissues, place mats and wet wipes. Other uses include, but are not limited to, oil absorbents, seed carriers, fillers for concrete, pressed board, and other construction materials, time released watering aids for house plants, and thin films.

The starch fibers of the present invention may be useful for forming fibrous structures and also forming absorbent materials, as described above. The absorbent structures/fibrous materials comprising the starch fibers of the present invention may have from a trace amount to one hundred percent (100%) starch fibers, or a blend of starch fibers and other suitable fibers. Other suitable fibers for the blend include cellulose fibers, synthetic fibers, and a combination thereof.

Starch polymers can include any naturally occurring (unmodified) starch, physically modified starch, chemically modified starch, biologically modified starch or combinations thereof.

Naturally occurring starch is generally a mixture of linear amylose and branched amylopectin polymer of D-glucose units. The amylose is a substantially linear polymer of D-glucose units joined by (1,4)- $\alpha$ -D links. The amylopectin is a highly branched polymer of D-glucose units joined by (1,4)- $\alpha$ -D links and (1,6)- $\alpha$ -D links at the branch points. Naturally occurring starch typically contains relatively high amylopectin, for example, corn starch (64-80% amylopectin), waxy maize (93-100% amylopectin), rice (83-84% amylopectin), potato (about 78% amylopectin), and wheat (73-83% amylopectin). Though all starches are useful herein, the present invention is

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most commonly practiced with high amylopectin natural starches derived from agricultural sources, which offer the advantages of being abundant in supply, easily replenishable and inexpensive in price.

Suitable naturally occurring starches can include, but are not limited to, corn starch, potato starch, sweet potato starch, wheat starch, sago palm starch, tapioca starch, rice starch, soybean starch, arrow root starch, bracken starch, lotus starch, waxy maize starch, high amylose corn starch, and commercial amylose powder. Naturally occurring starches particularly, corn starch and wheat starch, are the preferred starch polymers of choice due to their economy and availability.

Physically modified starch is formed by changing the dimensional structure. Physical modifications of the starch may be intramolecular or intermolecular modifications. Intramolecular modifications include reduced molecular weight and/or molecular weight distribution, changes in the polymer chain conformation, and the like. Intermolecular modifications include melting and/or disordering the starch molecules, reduction in crystallinity, crystallite size, and granular size, and the like. These physical modifications may be achieved by input of energy (such as thermal, mechanical, thermomechanical, electromagnetic, ultrasonic, and the like), pressure, moisture, fractionation, and combinations thereof. Physically modified starch can include  $\alpha$  starch, fractionated starch, moisture and heat treated starch.

Chemical modifications of starch typically include acid or alkali hydrolysis and oxidative chain scission to reduce molecular weight and molecular weight distribution. Suitable compounds for chemical modification of starch include organic acid such as citric acid, acetic acid, glycolic acid, and adipic acid; inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid boric acid, and partial salts of polybasic acids, e.g.,  $\text{KH}_2\text{PO}_4$ ,  $\text{NaHSO}_4$ ; group Ia or IIa metal hydroxides such as sodium hydroxide, potassium hydroxide; ammonia; oxidizing agents such as hydrogen peroxide, benzoyl peroxide, ammonium persulfate, potassium permagnate, sodium bicarbonate, hypochloric salts, and the like; and mixtures thereof. Preferred chemical agents or the present invention include ammonium persulfate, sulfuric acid, hydrochloric acid, and mixtures thereof.

Chemically modified starch may be formed by reaction of its OH

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groups with alkylene oxides, and other ether-, ester-, urethane-, carbamate-, or isocyanate- forming substances. Hydroxyalkyl, acetyl, or carbamate starches or mixtures thereof are preferred chemically modified starches. The degree of substitution of the chemically modified starch is 0.05 to 3.0, preferably 0.05 to 0.2.

5                   Biological modifications of starch include bacterial digestion of the carbohydrate bonds, or enzymatic hydrolysis using enzymes such as amylase, amylopectase, and the like.

                  The starch desirably has a bound water content of about 5% to 16% by weight of starch. A water content of 8% to 12% by weight of starch is particularly  
10               preferred. The amylose content of the starch is 0% to 80% by weight of starch, preferably 20% to 30% by weight of starch.

                  Natural, unmodified starch generally has a very high average molecular weight and a broad molecular weight distribution (e.g. natural corn starch has an average molecular weight of about 60,000,000 and a molecular weight distribution  
15               greater than 1000). The average molecular weight of starch can be reduced to the desirable range for the present invention by chain scission (oxidative or enzymatic), hydrolysis (acid or alkaline catalyzed), physical/mechanical degradation (e.g., via the thermomechanical energy input of the processing equipment), or combinations thereof. These reactions also reduce the molecular weight distribution of starch to less than  
20               about 600, preferably to less than about 300. The thermomechanical method and the oxidation method offer an additional advantage, carried out in situ of the melting spinning process.

                  In one embodiment, the natural starch is hydrolyzed in the presence of acids, such as hydrochloric acid or sulfuric acid, to reduce the molecular weight and  
25               molecular weight distribution. In another embodiment, a chain scission agent may be incorporated into the melt spinnable starch composition such that the chain scission reaction takes place substantially concurrently with the blending of the starch with other components. Nonlimiting examples of oxidative chain scission agents suitable for use herein include ammonium persulfate, hydrogen peroxide, hypochloric salts,  
30               potassium permanganate, and mixtures thereof. Typically, the chain scission agent is added in an amount effective to reduce the weight-average molecular weight of the



starch to the desirable range. For example, it is found that for uniaxial or biaxial melt attenuation processes, the starch should have a weight-average molecular weight ranging from about 1,000 to about 2,000,000, preferably from about 1,500 to about 800,000, more preferably from about 2,000 to about 500,000. It is found that compositions having modified starch in the above molecular weight range have a suitable melt shear viscosity, and thus, improved melt processability. The improved melt processability is evident in less interruptions of the process (e.g., reduced breakage, shots, defects, hang-ups) and better surface appearance and strength properties of the product.

Typically, the composition herein comprises from about 20 to about 99.99 wt%, preferably from about 30 to about 95 wt%, and more preferably from about 50 to about 85 wt%, of unmodified and/or modified starch. The weight of starch in the composition includes starch and its naturally occurring bound water content. It is known that additional free water may be incorporated as the polar solvent or plasticizer, and not included in the weight of the starch.

High molecular weight polymers (hereinafter "high polymers") which are substantially compatible with starch are also useful herein. The molecular weight of a suitable polymer should be sufficiently high to effectuate entanglements and/or associations with starch molecules. The high polymer preferably has a substantially linear chain structure. Though a linear chain having short (C1-C3) branches or a branched chain having one to three long branches are also suitable for use herein. As used herein, the term "substantially compatible" means when heated to a temperature above the softening and/or the melting temperature of the composition, the high polymer is capable of forming a substantially homogeneous mixture with the starch (i.e., the composition appears transparent or translucent to the naked eyes).

The Hildebrand solubility parameter ( $\delta$ ) can be used to estimate the compatibility between starch and the polymer. Generally, substantial compatibility between two materials can be expected when their solubility parameters are similar. It is known that water has a  $\delta_{\text{water}}$  value of  $48.0 \text{ MPa}^{1/2}$ , which is the highest among common solvents, probably due to the strong hydrogen bonding capacity of water. Starch typically has a  $\delta_{\text{starch}}$  value similar to that of cellulose (about  $34.4 \text{ MPa}^{1/2}$ ).

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Without being bound by theory, it is believed that polymer suitable for use herein preferably interact with the starch molecules on the molecular level in order to form a substantially compatible mixture. The interactions range from the strong, chemical type interactions such as hydrogen bonding between polymer and starch, to merely physical entanglements between them. The polymers useful herein are preferably high molecular weight, substantially linear chain molecules. The highly branched structure of an amylopectin molecule favors the branches to interact intramolecularly, due to the proximity of the branches within a single molecule. Thus, it is believed that the amylopectin molecule has poor or ineffective entanglements/interactions with other starch molecules, particularly other amylopectin molecules. The compatibility with starch enables suitable polymers to be intimately mixed and chemically interact and/or physically entangle with the branched amylopectin molecules such that the amylopectin molecules associate with one another via the polymers. The high molecular weight of the polymer enables it to simultaneously interact/entangle with several starch molecules. That is, the high polymers function as molecular links for starch molecules. The linking function of the high polymers is particularly important for starches high in amylopectin content. The entanglements and/or associations between starch and polymers enhance the melt extensibility of the starch composition such that the composition is suitable for extensional processes. In one embodiment, it is found that the composition can be melt attenuated uniaxially to a very high draw ratio (greater than 1000).

In order to effectively form entanglements and/or associations with the starch molecules, the high polymer suitable for use herein should have a weight-average molecular weight of at least 500,000. Typically the weight average molecular weight of the polymer ranges from about 500,000 to about 25,000,000, preferably from about 800,000 to about 22,000,000, more preferably from about 1,000,000 to about 20,000,000, and most preferably from about 2,000,000 to about 15,000,000. The high molecular weight polymers are preferred due to the ability to simultaneously interact with several starch molecules, thereby increases extensional melt viscosity and reduces melt fracture.

Suitable high polymers have a  $\delta$  polymer such that the difference

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between  $\delta$  starch and  $\delta$  polymer is less than about  $10 \text{ MPa}^{1/2}$ , preferably less than about  $5 \text{ MPa}^{1/2}$ , and more preferably less than about  $3 \text{ MPa}^{1/2}$ . Nonlimiting examples of suitable high polymers include polyacrylamide and derivatives such as carboxyl modified polyacrylamide, acrylics and acrylic polymers and copolymers including

5 polyacrylic acid, polymethacrylic acid, and their partial esters; vinyl polymers including polyvinyl alcohol, polyvinylacetate, polyvinylpyrrolidone, polyethylene vinyl acetate, polyethyleneimine, and the like; polyamides; polyalkylene oxides such as polyethylene oxide, polypropylene oxide, polyethylenepropylene oxide, and mixtures thereof. Copolymers made from mixtures of monomers selected from any of the

10 aforementioned polymers are also suitable herein. Other exemplary high polymers include water soluble polysaccharides such as alginates, carrageenans, pectin and derivatives, chitin and derivatives, and the like; gums such as guar gum, xanthum gum, agar, gum arabic, karaya gum, tragacanth gum, locust bean gum, and like gums; water soluble derivatives of cellulose, such as alkylcellulose, hydroxyalkylcellulose,

15 carboxymethylcellulose, and the like; and mixtures thereof.

Some polymers (e.g., polyacrylic acid, polymethacrylic acid) are generally not available in the high molecular weight range (i.e., 500,000 or higher). A small amount of crosslinking agents may be added to create branched polymers of suitably high molecular weight useful herein.

20 The high polymer is added to the composition of the present invention in an amount effective to visibly reduce the melt fracture and capillary breakage of fibers during the spinning process such that substantially continuous fibers having relatively consistent diameter can be melt spun. These polymers are typically present in the range from about 0.01 to about 10 wt%, preferably from about 0.03 to about 1

25 wt%, more preferably from about 0.05 to about 0.5 wt% of the composition. It is surprising to find that at a relatively low concentration, these polymers significantly improves the melt extensibility of the starch composition.

The starch compositions may optionally include additives to enhance melt flow and melt processability, particularly the extensibility of the composition

30 under the melt processing conditions. The additives may function as plasticizers and/or diluents to reduce the melt shear viscosity of the starch composition. The

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plasticizers are added to the composition of the present invention in an amount effective to improve the flow, hence, the melt processability. The plasticizers may also improve the flexibility of the final products, which is believed to be due to the lowering of the glass transition temperature of the composition by the plasticizer. The plasticizers should preferably be substantially compatible with the polymeric components of the present invention so that the plasticizers may effectively modify the properties of the composition. As used herein, the term "substantially compatible" means when heated to a temperature above the softening and/or the melting temperature of the composition, the plasticizer is capable of forming a substantially homogeneous mixture with starch (i.e., the composition appears transparent or translucent to the naked eye).

A plasticizer is typically added to the starch polymer in order to lower the glass transition temperature of the starch fibers thereby enhancing the flexibility of the fibers. In addition, the presence of the plasticizer lowers the melt viscosity which in turn facilitates the melt extrusion process. The plasticizer is advantageously an organic compound having at least one hydroxyl group, preferably a polyol. Without being bound by theory, it is believed that the hydroxyl groups of the plasticizers enhance compatibility by forming hydrogen bonds with the starch matrix material. Nonlimiting examples of useful hydroxyl plasticizers include sugars such as glucose, sucrose, fructose, raffinose, maltodextrose, galactose, xylose, maltose, lactose, mannose erythrose, glycerol, and pentaerythritol; sugar alcohols such as erythritol, xylitol, malitol, mannitol and sorbitol; polyols such as ethylene glycol, propylene glycol, dipropylene glycol, butylene glycol, hexane triol, and the like, and polymers thereof; and mixtures thereof.

Also useful herein as hydroxyl plasticizers are poloxomers (polyoxyethylene/polyoxypropylene block copolymers) and poloxamines (polyoxyethylene/polyoxypropylene block copolymers of ethylene diamine). Suitable "poloxomers" comprise block copolymers of polyoxyethylene/polyoxypropylene having the following structure:

$$\text{HO} - (\text{CH}_2 - \text{CH}_2 - \text{O})_x - (\text{CHCH}_3 - \text{CH}_2 - \text{O})_y - (\text{CH}_2 - \text{CH}_2 - \text{O})_z - \text{OH}$$
wherein x has a value ranging from about 2 to about 40, y has a value ranging from

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about 10 to about 50, and z has a value ranging from about 2 to about 40, and preferably x and z have the same value. These copolymers are available as Pluronic® from BASF Corp., Parsippany, NJ. Suitable poloxamers and poloxamines are available as Synperonic® from ICI Chemicals, Wilmington, DE, or as Tetronic® from  
5 BASF Corp., Parsippany, NJ.

Also suitable for use herein as hydroxyl-free plasticizers are other hydrogen bond forming organic compounds which do not have hydroxyl group, including urea and urea derivatives; anhydrides of sugar alcohols such as sorbitan; animal proteins such as gelatin; vegetable proteins such as sunflower protein, soybean  
10 proteins, cotton seed proteins; and mixtures thereof. All of the plasticizers may be use alone or in mixtures thereof.

Typically, the hydroxyl plasticizer comprises from about 5 wt% to about 70 wt%, more preferably from about 15 wt% to about 60 wt%, most preferably from about 30 wt% to about 40 wt% of the starch composition. The hydroxyl-free  
15 plasticizer typically comprises from about 0.1 wt% to about 70 wt%, preferably from about 5 wt% to about 65 wt%, more preferably from about 20 wt% to about 60 wt% of the starch composition.

In one embodiment, a mixture of the hydroxyl and hydroxyl-free plasticizers is used, wherein the hydroxyl plasticizers are sugars, such as sucrose, fructose, and sorbitol, and the hydroxyl-free plasticizers are urea and urea derivatives.  
20 It is found that urea and its derivatives in the starch composition of the present invention have a strong tendency to crystallize, that is, crystallization of urea and its derivatives occurs even under fast cooling condition such as melt blowing, spun bonding, melt extrusion, wet spinning, and the like. Therefore, urea and urea  
25 derivatives may be used as solidifying agents for modifying or controlling the solidification rate of the starch composition of the present invention. In a preferred embodiment, a mixture of sucrose and urea is added to the starch/polymer composition in an amount effective to achieve the desired melt processability and cooling rate.

Diluents may be added to the starch compositions of the present  
30 invention to adjust the melt shear viscosity and enhance the melt spinnability of the starch compositions. Generally, the melt shear viscosity decreases in a nonlinear

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manner as the polar solvent content is increased. Typically, the polar solvent is added in an amount from about 5 wt% to about 40 wt%, preferably from about 7 wt% to about 30 wt%, more preferably from about 10 wt% to about 20 wt%, of the total composition.

- 5                    Suitable for use herein as diluents are polar solvents having a solubility parameter  $\delta$  ranging from about 19 to about 48 MPa<sup>1/2</sup>, preferably from about 24 to about 48 MPa<sup>1/2</sup>, and more preferably from about 28 to about 48 MPa<sup>1/2</sup>. Nonlimiting examples include water, C1-C18 linear or branched alcohols, DMSO (dimethyl sulphoxide), formamide and derivatives such as N-methyl formamide, N-ethyl
- 10 formamide, acetamide and derivatives such as methyl acetamide, Cellosolv® (a glycol alkyl ether) and derivatives, such as butyl Cellosolv®, benzyl Cellosolv®, Cellosolv® acetate (all Cellosolv® and derivatives are available from J. T. Baker, Phillipsburg, NJ), hydrazine, and ammonia. It is also known that the  $\delta$  value of a solvent mixture can be determined by volume-averaging the  $\delta$  values of the individual solvents.
- 15 Therefore, mixed solvents having  $\delta$  values within the above-identified range (i.e., from about 19 to about 48 MPa<sup>1/2</sup>) are also suitable for use herein. For example, a mixed solvent of DMSO/water having a composition of 90/10 v/v would have a  $\delta$  value of about 28.5; such a mixed solvent system is suitable for use herein.

- It is found that polar solvents capable of forming hydrogen bonding are
- 20 more effective in lowering the melt viscosity of the composition. As such, a lower amount of the polar solvent is sufficient to adjust the viscosity to the desired range for melt spinning. Using a lower amount of the polar solvent provides a further advantage of reducing the need for an evaporation step during or subsequent to the melt processing step, which results in operating cost advantages such as lower energy
- 25 consumption, AND lower solvent recovery costs, as well as lower costs for environmental/regulatory compliance.

- The starch composition may optionally include liquid or volatile processing aids which function mainly as viscosity modifiers of the melt compositions. The processing aid is substantially volatilized and removed during the melt processing
- 30 stage such that only a residual/trace amount remains in the final product. Thus, they do not adversely affect the strength, modulus or other properties of the final product.

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The polar solvents disclosed above may also function as volatile processing aids. Other nonlimiting examples include carbonates such as sodium bicarbonate.

Optionally, other ingredients may be incorporated into the spinnable starch composition to modify the processability and/or to modify physical properties such as elasticity, tensile strength and modulus of the final product. Nonlimiting examples include cross-linking agents, emulsifiers, surfactants, lubricants, other processing aids, optical brighteners, antioxidants, flame retardants, dyes, pigments, fillers, proteins and their alkali salts, biodegradable synthetic polymers, waxes, low melting synthetic thermoplastic polymers, tackifying resins, extenders, and mixtures thereof. These optional ingredients may be present in quantities ranging from 0.1% to 70% by weight of the composition.

Exemplary biodegradable synthetic polymers include polycaprolactone; polyhydroxyalkanoates including polyhydroxybutyrates, and polyhydroxyvalerates; polylactides; and mixtures thereof.

Other additives are typically included with the starch polymer as a processing aid and to modify physical properties such as elasticity, dry tensile strength, and wet strength of the extruded fibers. Additives are typically present in quantities ranging from 0.1% to 70% by weight on a non-volatiles basis. Preferred additives are urea, urea derivatives, cross-linking agents, emulsifiers, surfactants, lubricants, proteins and their alkali salts, biodegradable synthetic polymers, waxes, low melting synthetic thermoplastic polymers, tackifying resins, extenders, and mixtures thereof. Preferred biodegradable synthetic polymers include polycaprolactone, polyhydroxybutyrates, polyhydroxyvalerates, polylactides, and mixtures thereof. Other preferred additives and associated properties include optical brighteners, antioxidants, flame retardants, dyes, pigments, and fillers. For the present invention, a preferred additive is urea in quantities ranging from 20% to 60% by weight.

Suitable extenders for use herein include gelatin, vegetable proteins such as sunflower protein, soybean proteins, cotton seed proteins, and water soluble polysaccharides; such as alginates, carrageenans, guar gum, agar, gum arabic and related gums, pectin, water soluble derivatives of cellulose, such as alkylcelluloses, hydroxyalkylcelluloses, carboxymethylcellulose, etc. Also, water soluble synthetic

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polymers, such as polyacrylic acids, polyacrylic acid esters, polyvinylacetates, polyvinylalcohols, polyvinylpyrrolidone, etc., may be used.

Lubricant compounds may further be added to improve the flow properties of the starch material during the processes used for producing the present invention. The lubricant compounds can include animal or vegetable fats, preferably in their hydrogenated form, especially those which are solid at room temperature. Additional lubricant materials include mono-glycerides and di-glycerides and phosphatides, especially lecithin. For the present invention, a preferred lubricant compound includes the mono-glyceride, glycerol mono-stearate.

Further additives including inorganic fillers such as the oxides of magnesium, aluminum, silicon, and titanium may be added as inexpensive fillers or processing aides. Additionally, inorganic salts, including alkali metal salts, alkaline earth metal salts, phosphate salts, etc., may be used as processing aides.

Other additives may be desirable depending upon the particular end use of the product contemplated. For example, in products such as toilet tissue, disposable towels, facial tissues and other similar products, wet strength is a desirable attribute. Thus, it is often desirable to add to the starch polymer cross-linking agents known in the art as "wet strength" resins.

A general dissertation on the types of wet strength resins utilized in the paper art can be found in TAPPI monograph series No. 29, Wet Strength in Paper and Paperboard, Technical Association of the Pulp and Paper Industry (New York, 1965). The most useful wet strength resins have generally been cationic in character. Polyamide-epichlorohydrin resins are cationic polyamide amine-epichlorohydrin wet strength resins which have been found to be of particular utility. Suitable types of such resins are described in U.S. Patent Nos. 3,700,623, issued on October 24, 1972, and 3,772,076, issued on November 13, 1973, both issued to Keim and both being hereby incorporated by reference. One commercial source of a useful polyamide-epichlorohydrin resin is Hercules, Inc. of Wilmington, Delaware, which markets such resins under the mark Kymene®.

Glyoxylated polyacrylamide resins have also been found to be of utility as wet strength resins. These resins are described in U.S. Patent Nos. 3,556,932,



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issued on January 19, 1971, to Coscia, et al. and 3,556,933, issued on January 19, 1971, to Williams et al., both patents being incorporated herein by reference. One commercial source of glyoxylated polyacrylamide resins is Cytec Co. of Stanford, CT, which markets one such resin under the mark Parex® 631 NC.

5                   It is found that when suitable cross-linking agent such as Parex® is added to the starch composition of the present invention under acidic condition, The composition is rendered water insoluble. That is, the water solubility of the composition, as tested by the Test Method described hereinafter, is less than 30%, preferably less than 20%, more preferably less than 10% and most preferably less than  
10   5%. The products such as fibers and films made from such a composition are also water insoluble.

                  Still other water-soluble cationic resins finding utility in this invention are urea formaldehyde and melamine formaldehyde resins. The more common functional groups of these polyfunctional resins are nitrogen containing groups such as  
15   amino groups and methylol groups attached to nitrogen. Polyethylenimine type resins may also find utility in the present invention. In addition, temporary wet strength resins such as Caldas® 10 (manufactured by Japan Carlit) and CoBond® 1000 (manufactured by National Starch and Chemical Company) may be used in the present invention.

20                   For the present invention, a suitable cross-linking agent is added to the composition in quantities ranging from about 0.1% by weight to about 10% by weight, more preferably from about 0.1% by weight to about 3% by weight.

#### The Rheology of The Starch Compositions

                  The rheological behavior of the starch composition is an important  
25   consideration for selecting suitable materials and fabrication equipment/processes. Many factors contribute to the rheological behavior of the starch composition, including the amount and the type of polymeric components used, the molecular weight and molecular weight distribution of the components, the amount and type of additives (e.g., plasticizers, processing aids), the processing conditions such as  
30   temperature, pressure, rate of deformation, and relative humidity, and in the case of non-Newtonian materials, the deformation history (i.e., a time or strain history

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dependence).

The starch composition of the present invention typically has a high solid content (i.e., a concentration above a critical concentration  $C^*$ ) such that a dynamic or fluctuating entangled network is formed wherein the starch molecules and the high polymers become associated and disassociated temporally. The association may be in the form of physical entanglements, van der Waals forces, or chemical interactions such as hydrogen bonding. The starch composition having the entangled network structure exhibits melt flow behavior typical of a non-Newtonian fluid.

The starch composition of the present invention may exhibit a strain hardening behavior, that is, the extensional viscosity increases as the strain or deformation increases. Typically, a Newtonian fluid exhibit a linear relationship between stress/force and strain. That is, there is no strain hardening behavior in a Newtonian fluid. On the other hand, a non-Newtonian fluid may exhibiting an increase in force at higher strain (i.e, strain hardening) while still exhibit a linear force - strain relationship at lower strain (i.e, Newtonian-like).

The strain experienced by a fluid element in a non-Newtonian fluid is dependent on its kinematic history, that is

$$\varepsilon = \int_0^t \dot{\varepsilon}(t') dt'$$

This time or history dependent strain is called the Hencky strain ( $\varepsilon_H$ ). For an ideal homogeneous uniaxial elongation, the strain rate experienced by every fluid element is equal to the strain imposed by the applied stress, such as the stresses applied externally by the instrument, device or process. In such an ideal case, the Hencky strain correlates directly with the sample deformation/elongation

$$\varepsilon_H = \ln (L/L_0)$$

Such an ideal strain response to applied stress is most often observed in Newtonian fluids.

The Trouton ratio ( $Tr$ ) is often used to express the extensional flow behavior. The Trouton ratio is defined as the ratio between the extensional viscosity ( $\eta_e$ ) and the shear viscosity ( $\eta_s$ ),

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$$Tr = \eta_e(\dot{\epsilon}, t) / \eta_s$$

wherein the extensional viscosity  $\eta_e$  is dependent on the deformation rate ( $\dot{\epsilon}$ ) and time (t). For a Newtonian fluid, the uniaxial extension Trouton ratio has a constant value of 3. For a non-Newtonian fluid, the extensional viscosity is dependent on the deformation rate ( $\dot{\epsilon}$ ) and time (t).

Shear viscosity ( $\eta_s$ ) relates to the melt processability of the starch composition using standard polymer processing techniques, such as extrusion, blow molding, compression molding, injection molding and the like. A starch composition having a shear viscosity, measured according to the Test Method disclosed hereinafter, of less than about 30 Pa•s, preferably from about 0.1 to about 10 Pa•s, more preferably from about 1 to about 8 Pa•s, is useful in the melt attenuation processes herein. Some starch compositions herein may have low melt viscosity such that they may be mixed, conveyed, or otherwise processed in traditional polymer processing equipment typically used for viscous fluids, such as a stationary mixer equipped with metering pump and spinneret. The shear viscosity of the starch composition may be effectively modified by the molecular weight and molecular weight distribution of the starch, the molecular weight of the high polymer, and the amount of plasticizers and/or solvents used. It is found that reducing the average molecular weight of the starch is an effective way to lower the shear viscosity of the composition.

It is generally known that melt shear viscosity is a material property useful for evaluating melt processability of the material in traditional thermoplastic processes such as injection molding or extrusion. For conventional fiber spinning thermoplastics such as polyolefins, polyamides and polyesters, there is a strong correlation between shear viscosity and extensional viscosity of these conventional thermoplastic materials and blends thereof. That is, the spinnability of the material can be determined simply by the melt shear viscosity, even though the spinnability is a property controlled primarily by melt extensional viscosity. The correlation is quite robust such that the fiber industry has relied on the melt shear viscosity in selecting and formulating melt spinnable materials. The melt extensional viscosity has rarely been used as an industrial screening tool.

It is therefore surprising to find that the starch compositions of the

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present invention do not exhibit such a correlation between shear and extensional viscosities. Specifically, when a high polymer selected according to the present invention is added to a starch composition, the shear viscosity of the composition remains relatively unchanged, or even decreases slightly. Based on conventional wisdom, such a starch composition would exhibit decreased melt processability and would not be suitable for melt extensional processes. However, it is surprisingly found that the starch composition herein shows a significant increase in extensional viscosity when even a small amount of high polymer is added. Consequently, the starch composition herein is found to have enhanced melt extensibility and is suitable for melt extensional processes (e.g., blow molding, spun bonding, blown film molding, foam molding, and the like).

Extensional or elongational viscosity ( $\eta_e$ ) relates to melt extensibility of the composition, and is particularly important for extensional processes such as fiber, film or foam making. The extensional viscosity includes three types of deformation: uniaxial or simple extensional viscosity, biaxial extensional viscosity, and pure shear extensional viscosity. The uniaxial extensional viscosity is important for uniaxial extensional processes such as fiber spinning, melt blowing, and spun bonding. The other two extensional viscosities are important for the biaxial extension or forming processes for making films, foams, sheets or parts. It is found that the properties of the high polymers have a significant effect on melt extensional viscosity. The high polymers useful for enhancing the melt extensibility of the starch composition of the present invention are typically high molecular weight, substantially linear polymers. Moreover, high polymers that are substantially compatible with starch are most effective in enhancing the melt extensibility of the starch composition.

It has been found that starch compositions useful for melt extensional processes typically have their extensional viscosity increased by a factor of at least 10 when a selected high polymer is added to the composition. Typically, the starch compositions of present invention show an increase in the extensional viscosity of about 10 to about 500, preferably of about 20 to about 300, more preferably from about 30 to about 100, when a selected high polymer is added.

It has also been found that melt processable compositions of the present

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invention typically have a Trouton ratio of at least about 3. Typically, the Trouton ratio ranges from about 10 to about 5,000, preferably from about 20 to about 1,000, more preferably from about 30 to about 500, when measured at 90 °C and 700 s<sup>-1</sup>.

When the starch composition of the present composition is subjected to an uniaxial extensional process, a draw ratio, expressed in  $(D_0^2/D^2)$  wherein  $D_0$  is the diameter of filament before drawing and  $D$  is the diameter of the drawn fiber, greater than 1000 can be easily achieved. The starch composition of the present invention typically achieves a draw ratio from about 100 to about 10,000, preferably greater than about 1,000, more preferably greater than about 3,000 and most preferably greater than about 5,000. More specifically, the starch composition of the present invention has sufficient melt extensibility to be melt drawn to fine fibers having a finite average diameter of less than 50 microns, preferably less than 25 microns, more preferably less than 15 microns, even more preferably less than 10 microns, and most preferably less than 5 microns.

When the starch composition of the present invention is subjected to a biaxial extensional process, the enhanced melt extensibility of the composition allows it to be melt drawn to films having a finite average caliper of less than 0.8 mils, preferably less than 0.6 mils, more preferably less than 0.4 mils, even more preferably less than 0.2 mils, and most preferably less than 0.1 mils.

The starch composition herein is processed in a flowable state, which typically occurs at a temperature at least equal to or higher than its melting temperature. Therefore, the processing temperature range is controlled by the melting temperature of the starch composition, which is measured according to the Test Method described in detail herein. The melting temperature of the starch composition herein ranges from about 80 to 180°C, preferably from about 85 to about 160°C, and more preferably from about 90 to about 140°C. It is to be understood that some starch compositions may not exhibit pure "melting" behavior. As used herein, the term "melting temperature" means the temperature or the range of temperature at or above which the composition melts or softens.

Exemplary uniaxial extensional processes suitable for the starch compositions include melt spinning, melt blowing, and spun bonding. These processes

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are described in detail in U. S. Patent No. 4,064,605, issued on December 27, 1977 to Akiyama et al.; U.S. Patent No. 4,418,026, issued on November 29, 1983 to Blackie et al.; U. S Patent No. 4,855,179, issued on August 8, 1989 to Bourland et al.; U. S. Patent No. 4,909,976, issued on March 20, 1990 to Cuculo et al.; U. S. Patent No. 5,145,631, issued on September 8, 1992 to Jezic; U.S. Patent No. 5,516,815, issued on May 14, 1996 to Buehler et al.; and U.S. Patent No. 5,342,335, issued on August 30, 1994 to Rhim et al.; the disclosure of all of the above are incorporated herein by reference. The resultant products may find use in filters for air, oil and water; vacuum cleaner filters; furnace filters; face masks; coffee filters, tea or coffee bags; thermal insulation materials and sound insulation materials; nonwovens for one-time use sanitary products such as diapers, feminine pads, and incontinence articles; biodegradable textile fabrics for improved moisture absorption and softness of wear such as microfiber or breathable fabrics; an electrostatically charged, structured web for collecting and removing dust; reinforcements and webs for hard grades of paper, such as wrapping paper, writing paper, newsprint, corrugated paper board, and webs for tissue grades of paper such as toilet paper, paper towel, napkins and facial tissue; medical uses such as surgical drapes, wound dressing, bandages, dermal patches and self-dissolving sutures; and dental uses such as dental floss and toothbrush bristles. The fibrous web may also include odor absorbants, termite repellants, insecticides, rodenticides, and the like, for specific uses. The resultant product absorbs water and oil and may find use in oil or water spill clean-up, or controlled water retention and release for agricultural or horticultural applications. The resultant starch fibers or fiber webs may also be incorporated into other materials such as saw dust, wood pulp, plastics, and concrete, to form composite materials, which can be used as building materials such as walls, support beams, pressed boards, dry walls and backings, and ceiling tiles; other medical uses such as casts, splints, and tongue depressors; and in fireplace logs for decorative and/or burning purpose.

The melt rheological behavior of the present starch composition also makes it suitable for use in conventional thermoplastic processes that involves biaxial extension of the material. By having the proper melt shear viscosity and biaxial extensional viscosity, the starch compositions of the present invention may

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substantially reduce the occurrence of tearing, surface defects, and other breakdowns or defects that interrupt continuous processes and produce unsatisfactory products. These processes include blow molding, blown film extrusion or coextrusion, vacuum forming, pressure forming, compression molding, transfer molding and injection molding. Nonlimiting examples of these processes are described in details in U.S. Patent No. 5,405,564, issued on April 11, 1995 to Stepto et al.; U.S. Patent No. 5,468,444, issued on November 21, 1995 to Yazaki et al.; U.S. Patent No. 5,462,982, issued on October 31, 1995 to Bastioli et al.; the disclosure of all of the above are hereby incorporated by reference. The articles produced by these processes include sheets, films, coatings, laminates, pipes, rods, bags, and shaped articles (such as bottles, containers). The articles may find use as bags such as shopping bags, grocery bags, and garbage bags; pouches for food storage or cooking; microwavable containers for frozen food; and pharmaceutical uses such as capsules or coatings for medicine. The films may be substantially transparent for use as food wraps, shrink wraps or windowed envelopes. The films may also be further processed for use as an inexpensive, biodegradable carrier for other materials such as seeds or fertilizers. Adhesives may be applied to the films or sheets for other uses such as labels.

The starch compositions of the present invention may also be made into a foamed structure by controlled removal of the volatile components (e.g., water, polar solvents). However, foaming or expanding agents are generally incorporated to produce articles having foamed or porous internal structure. Exemplary foaming or expanding agents include carbon dioxide, n-pentane, and carbonate salts such as sodium bicarbonate, either alone or in combination with a polymeric acid which has lateral carboxyl groups (e.g., polyacrylic acid, ethylene-acrylic copolymer). Nonlimiting examples of the foaming and forming processes are described in U. S. Patent No. 5,288,765, issued on February 22, 1994 to Bastioli et al.; U.S. Patent No. 5,496,895, issued on March 5, 1996 to Chinnaswamy et al.; U.S. Patent No. 5,705,536, issued on January 6, 1998 to Tomka; and U.S. Patent No. 5,736,586, issued on April 7, 1998 to Bastioli et al.; the disclosures of which are hereby incorporated by reference. The resultant products may find use in egg cartons; foamed cups for hot beverages; containers for fast food; meat trays; plates and bowls for one-time use such as at picnic

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or parties; packaging materials, either loose-fill or molded to conform to the packed article (e.g., a computer shipping package); thermal insulation materials; and noise insulation or sound proofing materials.

## (2) Exemplary Processes

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### Extruder Apparatus

The apparatus for carrying out the process of the invention consists of an extruder having

- a. first inlet chamber containing at least one conveying element,
- b. a heated receiving chamber downstream of said first chamber and  
10 containing at least one conveying element;
- c. a heated destructurization chamber, downstream of said second chamber, containing kneading and retaining elements;
- d. a heated degassing chamber under reduced pressure downstream of said destructurization chamber and said degassing chamber containing at least one  
15 conveying element, and
- e. a heated extrusion chamber downstream of said degassing chamber being under elevated pressure and having at least one conveying element.

Furthermore, the extruder preferably has at least one delivery device for solids for process step a, a liquid metering device for process step b, a degassing  
20 fitting for process step d, and a die for process step e. A twin screw extruder having closely meshing screws which run in the same direction is preferred.

For the present invention, the starch material can have a total water content, i.e. water of hydration plus added water, in the range of about 5 to about 40%; preferably in the range of about 10 to about 20%. The starch material is heated to  
25 elevated temperatures sufficient to form a pseudo-thermoplastic melt. Such temperature is typically higher than the glass transition and/or melting temperature of the formed material. For the present invention, the glass transition temperatures are at least about minus -30°C, preferably in the range of about -30°C to about 150°C, more preferably in the range of about -30°C to about 100°C, and most preferably in the  
30 range of about -30°C to about 25°C. The melting temperature is preferably in the range of about 100°C to about 180°C. The pseudo-thermoplastic melts of the



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invention are polymeric fluids having a shear rate dependent viscosity, as known in the art. The viscosity decreases with increasing shear rate as well as with increasing temperature.

The starch material is heated preferably in a closed volume in the presence of a low concentration of water to convert the starch material to a pseudo-thermoplastic melt. A closed volume can be a closed vessel or the volume created by the sealing action of the feed material as happens in the screw of extrusion equipment. Pressures created in a closed vessel will include pressures due to the vapor pressure of water as well as pressures generated due to compression of materials in the screw-barrel of the extruder.

A chain scission catalyst, which reduces the molecular weight by splitting the glycosidic bonds in the starch macromolecules resulting in a reduction of the average molecular weight of the starch, may be used to reduce the viscosity of the pseudo-thermoplastic melt. Suitable catalysts include inorganic and organic acids. Suitable inorganic acids include hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, and boric acid as well as the partial salts of polybasic acids, e.g.  $\text{NaHSO}_4$  or  $\text{NaH}_2\text{PO}_4$  etc. Suitable organic acids include formic acid, acetic acid, propionic acid, butyric acid, lactic acid, glycolic acid, oxalic acid, citric acid, tartaric acid, itaconic acid, succinic acid, and other organic acids known in the art, including partial salts of the polybasic acids. For the present invention, the preferred catalysts are hydrochloric acid, sulfuric acid, and citric acid, including mixtures thereof.

The reduction of the molecular weight of the non-modified starch used is by a factor of 2 to 5000, preferably by a factor of 4 to 4000. The concentration of catalysts is in the range of  $10^{-6}$  to  $10^{-2}$  mole of catalyst per mole of anhydro-glucose unit, preferably between  $0.1 \times 10^{-3}$  to  $5 \times 10^{-3}$  mole of catalyst per mole of anhydro-glucose unit of starch.

The following examples illustrate the type of extrusion equipment and operating parameters for producing starch fibers.

#### EXAMPLE 1

The purpose of this example is to illustrate starch fibers extruded at a particular cross section and subsequently drawn to a reduced cross section. Drawn

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pseudo-thermoplastic starch fibers were produced using a torque rheometer assembly 100 illustrated in Figure 1a. The torque rheometer assembly 100 includes a drive unit 110 (manufactured by Haake GmbH, model Rheocord 90), a barrel 120 partitioned into four temperature zones 122, 124, 126 and 128, a feed port 121, a single capillary die 130, and a simple mandrel winder 140. Twin screw elements 160 (model TW100, from Haake GmbH), depicted in Figure 1b, are attached to the drive unit 110 and disposed within the barrel 120. A capillary die was made to fit the die 130, with an orifice diameter of 0.5 mm and a length of 5.6 mm. The mandrel rewinder 140 comprises a 3 inch core mounted to a simple DC driven 3 inch diameter shaft. The 3 inch core can achieve surface speeds from 150 to 2000 fpm.

Raw materials utilized included the following:

45% by weight Durabond A Corn Starch from National Starch

25% by weight Water

15% by weight Urea available from Aldrich Chemicals

15% by weight Sorbitol available from Aldrich Chemicals

All raw materials were mixed off-line until a slurry was formed. The slurry was then manually fed into the feed port 121 of the torque rheometer assembly 100.

The settings on the torque rheometer were as follows:

RPM	50
Barrel Temperature	110 °C
Die Temperature	105 °C
Feed Rate	1.7 grams/minute

After running the rheometer for approximately 20 minutes, the process stabilized and a single pseudo-thermoplastic starch fiber 150 exited the die 130. The single fiber 150 was manually wound around the mandrel winder 140. The winder 140 was then slowly sped up to 900 feet/minute surface speed in order to draw the fiber 150 increasing the fiber length and decreasing the cross sectional area. The diameter of the wound fiber 150 was between 70 and 90 microns.

## EXAMPLE 2

The purpose of this example is to illustrate how starch fibers can be arranged to



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The pitch of the screw is the distance needed for a flight to complete one revolution of the core. It is expressed as the number of screw element diameters per one complete revolution of a flight. Decreasing the pitch of the screw increase the pressure generated by the screw and decreases the volumetric capacity of the screw.

5        The length of a screw element is reported as the ratio of length of the element divided by the diameter of the element.

      This example uses TLS and SLS. Screw element 310 is a TLS with a 1.0 pitch and a 1.5 length ratio. Screw element 320 is a TLS with a 1.0 pitch and a 1.0 L/D ratio. Screw element 340 is a SLS with a  $\frac{1}{4}$  pitch and a 1.0 length ratio. Screw  
10    element 350 is a SLS and a  $\frac{1}{4}$  pitch and a  $\frac{1}{2}$  length ratio.

      Bilobal paddles 360 serving as mixing elements are also included in a series with the SLFS and TLFS screws in order to enhance mixing. Various configurations of bilobal paddles 360 and reversing elements 340 and 350 are used in order to control flow and corresponding mixing time.

15        In zone 1, Durabond A starch and sorbitol are fed into the solid feed port 204 and urea is fed into the liquid port 208 forming a mixture with a 60/20/20 weight ratio. These materials are combined inside the extruder with water added at the liquid feed port 206 to form a pseudo-thermoplastic melt. The temperature, pressure, and  
      corresponding function of each zone are provided in Table I.

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Table I

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Zone	Temperature (deg F)	Pressure (gauge PSI)	Description of Screw
1	70	0	Feeding
2	193	34	Mixing
3	268	0	Mixing
4	210	0	Pressure Decreasing Conveying
5	205	0-10	Pressure Generating
Die	194	430	Shaping

EXAMPLE 4STARCH FIBERS EXTRUDED WITH A NON-VENTED TWIN SCREW  
EXTRUDER

The purpose of this example is to illustrate a non-vented twin screw extruder configuration, depicted in Figure 3a, used to make starch fibers for the present invention. Starch fibers are made using an APV Baker (Peterborough, England) twin screw extruder 200, a capillary die 212, and a winder (not shown).

The non-vented twin screw extruder configuration is illustrated in Figure 3a. The twin screw extruder comprises a barrel 202 that is separated into five zones. The barrel 202 encloses the extrusion screws and mixing elements and serves as a containment vessel during the extrusion process. A solid feed port 204 is disposed in zone 1 and liquid feed ports 206, and 208 are disposed in zone 1 and zone 2.

The screw and mixing element configuration for the twin screw extruder is illustrated in Figure 3b.

In zone 1, Durabond A starch and sorbitol are fed into the solid feed port 204 and urea is fed into the liquid port 208 forming a mixture with a 60/20/20 weight ratio. These materials are combined inside the extruder with water added at the liquid feed port 206 to form a pseudo-thermoplastic melt. The temperature, pressure, and corresponding function of each zone are provided in Table II.

Table II

Zone	Temperature (deg F)	Pressure (gauge PSI)	Description of Screw
1	70	0	Feeding
2	180	0	Mixing
3	260	0	Mixing
4	215	0	Pressure Decreasing Conveying
5	193	30	Pressure Generating
Die	172	150	Shaping

EXAMPLE 5  
FOAMED STARCH FIBERS EXTRUDED WITH A NON-VENTED TWIN  
SCREW EXTRUDER

The purpose of this example is to illustrate the various zones of a twin screw extruder without a vent and the operating parameters associated with each zone for producing foamed starch fibers which are lower in density and having a higher absorbent capacity relative to non-foamed starch fibers. Foamed starch fibers are made using a fiber making apparatus comprising the twin screw extruder configuration depicted in Figures 3a and 3b.

In zone 1, Durabond A starch and sorbitol are fed into the solid feed port 204 and urea is fed into the liquid port 208 forming a mixture with a 60/20/20 weight ratio. These materials are combined inside the extruder with water added at the liquid feed port 206 to form a pseudo-thermoplastic melt. The temperature, pressure, and corresponding function of each zone are provided in Table III.

TABLE III

Zone	Temperature (deg F)	Pressure (gauge PSI)	Description of Screw
1	70	0	Feeding
2	180	0	Mixing
3	260	0	Mixing
4	240	0	Pressure Decreasing Conveying
5	220	30	Pressure Generating
Die	225	150	Shaping

Pseudo-thermoplastic Starch Melt Fiber Spinning

The production of fibers according to the invention from the pseudo-thermoplastic melt compositions occurs by the usual melt spinning processes. Devices for producing non-woven thermoplastic fabric structures from extruded polymers are well known in the art. Extruded polymers under pressure, are forced through a spinneret forming a vertically oriented curtain of downward advancing fibers. The fibers are quenched with air in conjunction with a suction-type drawing or attenuating air slot. U.S. Pat. No. 5,292,239 issued to Zeldin, et al., March 8, 1994, discloses a device that reduces significant turbulence in the air flow in order to uniformly and

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consistently apply a drawing force to the fibers.

For the present invention, structures are produced from a mixture comprising starch, water, plasticizers, and other optional additives. As shown in Figure 4, the mixture is converted to a pseudo-thermoplastic melt in an extruder and conveyed through a spinneret 10 to a drawing unit 20 forming a vertically oriented curtain of downward advancing fibers F.

The spinneret 10 comprises an assembly which is known in the art. The spinneret 10 includes a plurality of nozzle bores 12 with hole diameters customary for fiber production. The spinneret assembly 10 can be adapted to the fluidity of the melt so that every nozzle bore 12 has the same rate of flow.

The drawing unit 20 comprises an open upper end 22, an open lower end 24, and an air supply manifold 26 supplying compressed air to internal nozzles (not shown) oriented in a downward direction. As compressed air flows through the internal nozzles, air is drawn into the open upper end 22 of the drawing unit 20 forming a rapidly moving stream of air flowing in the downward direction. The air stream produces a drawing force on the fibers causing them to be attenuated or stretched before exiting the open lower end 24 of the drawing unit 20.

For the present invention, the fibers exiting the drawing unit 20 can have a size ranging from about 0.01 decitex to about 135 decitex. Preferably, the fibers exiting the drawing unit 20 have a size ranging from about 0.02 decitex to about 30 decitex. Most preferably, the fibers exiting the drawing unit 20 have a size ranging from about 0.02 decitex to about 5 decitex.

Upon exiting the drawing unit 20, the fibers are deposited on a moving conveyor belt 30 to form flexible, low density structure comprising fibers. The fibers are then joined to each other through conventional techniques. A preferred process for producing structures of the present invention is described in U.S. Pat. No. 5,688,468 issued to Lu, November 18, 1997, which is incorporated herein by reference.

In addition to spunbonded structures, mono-fibers, multi-fibers, staple fibers, hollow fibers, shaped fibers, such as multi-lobal fibers and multi-component fibers can all be produced by using the compositions and methods of the present invention. The process for the production of these fibers may be in one stage with a

compounding extruder producing a pseudo-thermoplastic starch melt and conveying it without cooling through a melt filter to a spinneret. Staple starch fibers may also be converted to flexible, low density structures by carding, air laying, and similar processes known in the art.

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### (3) MATERIAL PROPERTIES

Products such as disposable towels, toilet tissue, facial tissue, napkins and wet wipes manifest various physical characteristics which include basis weight and apparent density, both of which have been previously defined. For the present invention, the structure comprising pseudo-thermoplastic starch fibers can have a basis weight ranging from about 10 g/m<sup>2</sup> to about 450 g/m<sup>2</sup>. More preferably, the structure can have a basis weight ranging from about 12 g/m<sup>2</sup> to about 150 g/m<sup>2</sup>. Moreover, the structure of the present invention can have an apparent density ranging from about 0.02 g/cm<sup>3</sup> to about 0.20 g/cm<sup>3</sup>; more preferably, an apparent density ranging from about 0.04 g/cm<sup>3</sup> to about 0.15 g/cm<sup>3</sup> and most preferably, an apparent density ranging from about 0.04 g/cm<sup>3</sup> to about 0.12 g/cm<sup>3</sup>.

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The products listed above also exhibit certain mechanical properties, particularly, strength, flexibility, and absorbency. Measures of strength include geometric mean dry tensile strength (GMDT), and geometric mean wet tensile strength (GMWT) wherein GMWT includes initial wet tensile strength and decayed wet tensile strength. Flexibility is related to stiffness and can attribute to softness. Absorbency relates to the products' ability to take up fluids as well as the capacity to retain them. Geometric mean dry tensile strength (GMDT), previously defined, provides a measure of the dry tensile strength of the structure. The method used to determine this measure is described below. For the present invention, the structure comprising pseudo-thermoplastic starch fibers can have a GMDT ranging from about 10 g/cm to about 1200 g/cm. More preferably, the structure can have a GMDT ranging from about 30 g/cm to about 600 g/cm. Most preferably, the structure can have a GMDT ranging from about 40 g/cm to about 475 g/cm.

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Geometric mean wet tensile strength (GMWT), previously defined, provides a measure of the wet tensile strength of the structure. The initial geometric mean tensile strength is the wet tensile strength of a structure after it has been

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immersed in water for five seconds. The method used to determine this measure is described below. For the present invention, the structure comprising pseudo-thermoplastic starch fibers can have a GMWT ranging from about 2 g/cm to about 400 g/cm. More preferably, the structure can have a GMWT ranging from about 2 g/cm to about 200 g/cm.

Geometric mean decayed wet tensile strength (GMDWT) is a measure of the wet tensile strength of the structure after being immersed in water for thirty minutes. For the present invention, the structure comprising pseudo-thermoplastic starch fibers can have a GMDWT ranging from about 0 g/cm to about 20 g/cm. More preferably, the structure can have a GMDWT ranging from about 0 g/cm to about 10 g/cm.

Softness has been described as a physiologically perceived attribute which is generally measured by expert or non-expert panel evaluations. Perceived softness can be broken down into two components; bulk softness and surface softness. Bulk softness has been correlated to sheet stiffness and flexibility while surface softness has been related to surface texture and smoothness. High softness requires flexibility. The method used for determining the total flexibility of a structure is defined below. For the present invention, the structure has a total flexibility ranging from about 1.0 g/cm to about 75 g/cm; preferably from about 2.0 g/cm to about 50 g/cm; and more preferably from about 2.0 g/cm to about 35 g/cm.

Products such as disposable towels, toilet tissue, facial tissue, napkins, and wet wipes require a certain level of absorbency. Herein, absorbency means absorbent capacity which is a measure of the amount of distilled water absorbed and retained by the structure. The method used for determining the absorbency of a structure is defined below. For the present invention, the structure has an absorbency ranging from about

1  $\frac{\text{g}_{\text{Water}}}{\text{g}_{\text{Dry Structure}}}$  to

about 15  $\frac{\text{g}_{\text{Water}}}{\text{g}_{\text{Dry Structure}}}$ ; preferably from about 2  $\frac{\text{g}_{\text{Water}}}{\text{g}_{\text{Dry Structure}}}$  to about 14  $\frac{\text{g}_{\text{Water}}}{\text{g}_{\text{Dry Structure}}}$ ; more preferably from about 3  $\frac{\text{g}_{\text{Water}}}{\text{g}_{\text{Dry Structure}}}$  to about 13  $\frac{\text{g}_{\text{Water}}}{\text{g}_{\text{Dry Structure}}}$ .

#### (4) ANALYTICAL METHODS

##### (a) Sample Conditioning And Preparation:

Prior to testing, samples are conditioned at a relative humidity of 48% to 50% and within a temperature range of 22°C to 24°C until a moisture content of  
5 from about 5% to about 16% by weight as measured by TGA (Thermo Gravimetric Analysis) is achieved. For Thermo Gravimetric Analysis, a Hi-res. TGA2950 Termogravimetric analyzer from TA Instruments is used. Approximately 20 mg of sample is weighed into a TGA pan. Following the manufacturer's instructions, the sample and pan are inserted into the unit and the temperature is increased at a rate of  
10 10°C/minute to 250°C. The % moisture in the sample is determined using the weight lost and the initial weight as follows:

$$\% \text{ Moisture} = \frac{\text{Start Weight} - \text{Weight @ } 250^{\circ}\text{C}}{\text{Start Weight}} \cdot 100\%$$

where all weights are in milligrams.

##### 15 (b) Basis Weight

One stack of 8 plies is made from the preconditioned samples. The stack of 8 plies is cut into a 4 inch by 4 inch square. A rule die from Acme Steel Rule Die Corp. (5 Stevens St. Waterbury Conn., 06714) is used to accomplish this cutting. For the actual measurement of the weight of the sample, a top loading balance with a  
20 minimum of 0.01 g readability is used. The stack of 8 plies is laid on the pan of the top loading balance. The balance is protected from air drafts and other disturbances using a draft shield. Weights are recorded when the readings on the balance become constant. Weights are measured in grams.

The weight reading is divided by the number of plies tested. The  
25 weight reading is also divided the weight reading by the area of the sample which is normally 16 square inches, which is approximately equal to 0.0103 square meters. The unit of measure for basis weight as used herein is grams/square meter. This is calculated using the 0.0103 square meter area noted above.

##### (c) Caliper

30 Preconditioned samples are cut to a size greater than the size of the foot used to measure the caliper. The foot to be used is a circle with an area of 3.14 square inches.

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The sample is placed on a horizontal flat surface and confined between the flat surface and a load foot having a horizontal loading surface, where the load foot loading surface has a circular surface area of about 3.14 square inches and applies a confining pressure of about 15 g/square cm (0.21 psi) to the sample. The caliper is the  
5 resulting gap between the flat surface and the load foot loading surface. Such measurements can be obtained on a VIR Electronic Thickness Tester Model II available from Thwing-Albert, Philadelphia, Pa. The caliper measurement is repeated and recorded at least five times. The result is reported in millimeters.

The sum of the readings recorded from the caliper tests is divided by the  
10 number of readings recorded. The result is reported in millimeters (mm).

(d) Dry Tensile Strength

The dry tensile strength is determined on one inch wide strips of sample using a Thwing-Albert Intellect II Standard Tensile Tester (Thwing-Albert Instrument Co., 10960 Dutton Rd., Philadelphia, Pa., 19154). This method is intended for use on  
15 finished paper products, reel samples, and unconverted stocks.

Two stacks of 8 plies are made from the preconditioned samples. From one of these stacks of 8 plies, four strips are cut 1 inch by 7 inch with the long 7 inch dimension running parallel to the machine direction. Note these samples are machine direction samples. An additional four strips 1 inch by 7 inch with the long 7  
20 inch dimension running parallel to the cross direction. All cuts are made using a cutter (JDC-1-10 or JDC-1-12 with safety shield from Thwing-Albert Instrument Co., 10960 Dutton Road, Philadelphia, Pa., 19154). A total of eight samples are produced: four 1 inch by 7 inch strips, 8 plies thick, with the 7 inch dimension running parallel to the machine direction and four 1 inch by 7 inch strips, 8 plies thick, with the 7 inch  
25 dimension running parallel to the cross direction.

Each of the four eight ply stacks of machine direction and cross machine direction sample tensile strips are measured in the Thwing-Albert Intellect II Standard Tensile Tester. The four measurements of the 8 ply stacks of machine direction sample tensile strips are summed and divided by four, which is the number of  
30 machine direction strips tested. The sum is also divided by eight, which the number of usable units per tensile strip. The calculation is repeated for the cross machine

direction measurements.

All results are in units of grams/inch. Appropriate unit conversions may be made to achieve units of grams/cm as reported herein.

(e) Initial Wet Tensile Strength

5 For the initial wet tensile strength determination, a portion of the test sample is immersed in water for five seconds prior to the tensile strength measurement. The wet tensile strength is determined on one inch wide strips of sample using a Thwing-Albert Intelect II Standard Tensile Tester (Thwing-Albert Instrument Co., 10960 Dutton Rd., Philadelphia, Pa., 19154) and a Finch Wet Strength Device,  
10 Catalog Number 731D (Thwing-Albert Instrument Co., 10960 Dutton Rd., Philadelphia, Pa., 19154).

Prior to sample preparation and wet tensile testing, the samples should be cured in a forced draft oven at  $105 \pm 3$  degree Celsius for a period of 5 minutes  $\pm$  10 seconds. The samples should be suspended in the oven such that the forced air can  
15 circulate between them.

Sample preparation and all aspects of the wet tensile testing should take place within the confines of the constant temperature and humidity room. Two stacks of 5 plies each are made from the cured samples after conditioning. From one of these stacks of 5 plies, four strips are cut 1 inch by 4 inch with the long 4 inch dimension  
20 running parallel to the machine direction for machine direction samples. An additional four strips are cut 1 inch by 4 inch with the long 4 inch dimension running parallel to the cross direction for cross direction samples. All cuts are made using a paper cutter (JDC-1-10 or JDC-1-12 with safety shield from Thwing-Albert Instrument Co., 10960 Dutton Road, Philadelphia, Pa., 19154). There are a total of eight samples: four 1 inch  
25 by 4 inch strips which are 5 plies thick with the 4 inch dimension running parallel to the machine direction and four 1 inch by 4 inch strips which are 5 plies thick with the 4 inch dimension running parallel to the cross direction.

Each of the four five ply stacks of machine direction and cross machine direction sample tensile strips are measured in the Thwing-Albert Intelect II Standard  
30 Tensile Tester. The four measurements of the 5 ply stacks of machine direction sample tensile strips are summed and divided by four, which is the number of machine

- 40 -

direction strips tested. The sum is also divided by five, which the number of usable units per tensile strip. The calculation is repeated for the cross machine direction measurements.

5 All results are in units of grams/inch. Appropriate unit conversions may be made to achieve units of grams/cm as reported herein.

(f) Decayed Wet Tensile (Soaked for 30 minutes)

Same as the Initial Wet Tensile Strength except the samples are allowed to soak in the water for 30 minutes ( $\pm 30$  seconds) prior to Wet Tensile Strength Testing.

10 (g) Flexibility

Flexibility as used herein is defined as the slope of the secant of the graph-curve derived from force vs. stretch % data which secant passes through the origin (zero % stretch, zero force) and through the point on the graph-curve where the force per centimeter of width is 20 grams. For example, for a sample which stretches  
15 10% (i.e., 0.1 cm/cm of length) with 20 grams of force per cm of sample width, the slope of the secant through (0%, 0) and (10%, 20) is 2.0 using the formula:

$$\text{Slope} = \frac{Y_2 - Y_1}{X_2 - X_1}$$

Total Flexibility as used herein means the geometric mean of the  
20 machine-direction flexibility and cross-machine-direction flexibility. Mathematically, this is the square root of the product of the machine-direction flexibility and cross-machine-direction flexibility in grams per cm.

(h) Absorbency

Absorbency herein is defined as the amount (grams) of distilled water at  
25  $73 \pm 2$  °F per gram of sample held by the sample after it has been submerged in a water bath for a period of  $30 \pm 3$  seconds and then allowed to sit in a horizontal position for  $120 \pm 5$  seconds followed by  $60 \pm 5$  seconds sitting at a  $75^\circ$  angle (as measured off of horizontal).

A preconditioned sample is cut to a size of 11 inches by 11 inches. The  
30 Machine Direction of the sample is marked and the sample is weighed on a torsion balance to  $\pm 0.01$  grams and recorded. This is known as the Sample Dry Weight. After weighing the sample, the dry sample rack (further described below) is placed on

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the balance and the weight is recorded to  $\pm 0.01$  grams. This is known as the Rack Dry Weight.

The sample is placed on a rack and covered with a rack cover, further described below. The sample, contained by the rack and rack cover, is gently and  
5 completely submerged (to a depth of 2 to 3 inches) horizontally in a bath of distilled water at a temperature of  $73 \pm 2$  °F for  $30 \pm 3$  seconds.

After being submerged for  $30 \pm 3$  seconds, the sample is gently raised (horizontally), the rack cover is gently removed, and the sample and rack are allowed to sit for a period of  $120 \pm 5$  seconds in order to drain. While the sample is sitting in  
10 the horizontal position, water sitting on the rack is gently wiped off without touching the sample.

Following the drying of the rack and the completion of the horizontal sitting period, the rack and sample together are gently raised so that the Machine Direction is at an angle of  $75^\circ$  from horizontal and allowed to sit in this position for a  
15 period of  $60 \pm 5$  seconds. After this sitting period is completed, the rack and sample are returned to a horizontal position and once again the rack is dried of standing water. The rack and sample are gently placed on the balance and the weight  $\pm 0.01$  grams is recorded. This is known as the Sample and Rack Wet Weight.

The absorbency measurement is made and recorded for three (3)  
20 machine direction samples and three (3) cross machine direction samples. During the cross machine direction measurement, the cross-machine direction of the sample is placed at an angle of  $75^\circ$  from horizontal.

An illustration of the sample rack and cover is shown in Figure 5. Both include frames 400 constructed of 16 GA Aluminum (Teflon Coated after Fabrication)  
25 with a cross-section shown in Figure 6. The outside dimensions 405, 410 of the frames 400 are about 13.75 inches by about 16.75 inches. Nylon thread 420 (0.3mm diameter) is tightly strung across the Aluminum frames 400 in a pattern shown in Figure 5. All diagonal threads go over those threads running perpendicular and/or parallel to the frames 400.

30 For each of the 6 tests, the following calculation is made (all units are grams):

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Sample Wet Weight = Sample and Rack Wet Weight - Rack Dry Weight

$$\text{Absorbency} = \frac{(\text{Sample Wet Weight} - \text{Sample Dry Weight})}{\text{Sample Dry Weight}}$$

- 5                    The calculation is repeated for each of the 6 measurements and all 6 absorbency numbers are averaged together and reported as  $\frac{g_{\text{Water}}}{g_{\text{Dry Structure}}}$  (grams of water / grams of sample dry weight).

(i) SHEAR VISCOSITY

- 10                    The shear viscosity of the composition is measured using a rotational viscometer (Model DSR 500, manufactured by Rheometrics). A preheated sample composition is loaded into the barrel section of the rheometer, and substantially fills the barrel section (about 60 grams of sample is used). The barrel is held at a test temperature of 90°C. After the loading, air generally bubbles to the surface and does create problems for the run. For a more viscous samples, compaction prior to running the test may be used to rid the molten sample of entrapped air. The viscometer is
- 15                    programmed to ramp the applied stress from 10 dyne/cm to 5000 dyne/cm. The strain experienced by the sample is measure by a strain gauge. The apparent viscosity of the composition can be derived therefrom. Then log (apparent shear viscosity) is plotted against log (shear rate) and the plot is fitted by the power law  $\eta = K \gamma^{n-1}$ , wherein K is
- 20                    a material constant,  $\gamma$  is the shear rate. The reported shear viscosity of the starch composition herein is an extrapolation to a shear rate of 700 s<sup>-1</sup> using the power law relation.

(j) EXTENSIONAL VISCOSITY

- 25                    The extensional viscosity is measured using a capillary rheometer (Model Rheograph 2003, manufactured by Geottfert). The measurements are conducted using an orifice die having a diameter D of 0.5 mm and a length L of 0.25 mm (i.e., L/D = 0.5). The die is attached to the lower end of a barrel, which is held at a test temperature of 90°C. A preheated sample composition is loaded into the barrel section of the rheometer, and substantially fills the barrel section. After the loading,
- 30                    air generally bubbles to the surface and does create problems for the run. For more viscous compositions, compaction prior to running the test may be used to rid the molten sample of entrapped air. A piston is programmed to push the sample from the

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barrel through the orifice die at a chosen rate. As the sample goes from the barrel through the orifice die, the sample experiences a pressure drop. An apparent viscosity can be obtained from the pressure drop and the flow rate of the sample through the orifice die. Corrections are often applied to the apparent viscosity following  
5 procedures generally known in the art. A shear correction factor and Cogswell equation are applied to the calculation of the extensional viscosity. The corrected extensional viscosity at  $700 \text{ s}^{-1}$  is reported.

It is known that the extensional viscosity can be measured using an orifice die and applying the correction factors, following the method described herein.  
10 More details of extensional viscosity measurements are disclosed in S. H. Spielberg et al., The Role Of End-Effects On Measurements Of Extensional Viscosity In Filament Stretching Rheometers, Journal of Non-Newtonian Fluid Mechanics, Vol. 64, 1996, p. 229-267; Bhattacharya, et al., Uniaxial Extensional Viscosity During Extrusion Cooking From Entrance Pressure Drop Method, Journal of Food Science, Vol. 59, No.  
15 1, 1994, p. 221-226; both are hereby incorporated by reference. It is also known that the extensional viscosity can be measured using a hyperbolic or semi-hyperbolic die. Detailed disclosure of extensional viscosity measurements using a semi-hyperbolic die is disclosed in U.S. Patent No. 5,357,784, issued October 25, 1994 to Collier, the disclosure of which is incorporated herein by reference.

20 (k) MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION

The weight-average molecular weight ( $M_w$ ) and molecular weight distribution (MWD) of starch are determined by Gel Permeation Chromatography (GPC) using a mixed bed column. Parts of the instrument are as follows:

25	Pump	Waters Model 600E
	System controller	Waters Model 600E
	Autosampler	Waters Model 717 Plus
	Column	PL gel 20 $\mu\text{m}$ Mixed A column (gel molecular weight ranges from 1,000 to 30 40,000,000) having a length of 600 mm and an internal diameter of 7.5 mm.





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standard, which has an melting temperature (onset) of 156.6°C and a heat of melting of 6.80 calories per gram, as reported in the chemical literature. Standard DSC operating procedure per manufacturer's Operating Manual is used. Due to the volatile evolution (e.g., water vapor) from the starch composition during a DSC measurement, a high  
5 volume pan equipped with an o-ring seal is used to prevent the escape of volatiles from the sample pan. The sample and an inert reference (typically an empty pan) are heated at the same rate in a controlled environment. When an actual or pseudo phase change occurs in the sample, the DSC instrument measures the heat flow to or from the sample versus that of the inert reference. The instrument is interfaced with a computer  
10 for controlling the test parameters (e.g., the heating/cooling rate), and for collecting, calculating and reporting the data.

The sample is weighed into a pan and enclosed with an o-ring and a cap. A typical sample size is 25-65 milligrams. The enclosed pan is placed in the instrument and the computer is programmed for the thermal measurement as follows:

- 15                   1.                equilibrate at 0°C;
2.                hold for 2 minutes at 0°C;
3.                heat at 10°C/min to 120°C;
4.                hold for 2 minutes at 120°C;
5.                cool at 10°C/min to 30°C;
- 20                   6.                equilibrate at ambient temperaure for 24 hours, the  
                                  sample pan may be removed from the DSC instrument  
                                  and placed in a controlled environment at 30°C in this  
                                  duration;
7.                return sample pan to the DSC instrument and equilibrate  
25                                   at 0°C;
8.                hold for 2 minutes;
9.                heat at 10°C/min to 120°C;
10.              hold for 2 minutes at 120°C;
11.              cool at 10°C/min to 30°C and equilibrate; and
- 30                   12.              remove the used sample.

The computer calculates and reports the thermal analysis result as

differential heat flow ( $\Delta H$ ) versus temperature or time. Typically the differential heat flow is normalized and reported on per weight basis (i.e, cal/mg). Where the sample exhibits a pseudo phase transition, such as a glass transition, a differential of the  $\Delta H$  v. time/temperature plot may be employed to more easily determine a glass transition temperature.

(m) WATER SOLUBILITY

A sample composition is made by mixing the components with heat and stirring until a substantially homogeneous mixture is formed. The melt composition is cast into a thin film by spreading it over a Teflon® sheet and cooling at ambient temperature. The film is then dried completely (i.e., no water in the film/composition) in an oven at 100°C. The dried film is then equilibrated to room temperature. The equilibrated film is ground into small pellets.

To determine the % solids in the sample, 2 to 4 grams of the ground sample is placed in a pre-weighed metal pan and the total weight of pan and sample is recorded. The weighed pan and sample is palced in a 100°C oven for 2 hours., and then taken out and weighed immediately. The % solids is calculated as follows:

$$\% \text{ Solids} = \frac{(\text{dried weight of ground sample \& pan} - \text{weight of pan})}{(\text{first weight of ground sample \& pan} - \text{weight of pan})} \times 100$$

To determine the solubility of the sample composition, weigh 10 grams of ground sample in a 250mL beaker. Add deionized water to make a total weight of 100 grams. Mix the sample and water on a stir plate for 5 minutes. After stirring, pour at least 2mL of stirred sample into a centrifuge tube. Centrifuge 1 hour at 20,000g at 10°C. Take the supernatant of the centrifuged sample and read the refractive index. The % solubility of the sample is calculated as follows:

$$\% \text{ Soluble Solids} = \frac{(\text{Refractive Index \#}) \times 1000}{\% \text{ Solids}}$$

EXAMPLES

The materials used in the Examples are as follows:

Crystal Gum® is a modified starch having a weight-average molecular weight of 100,000; Nadex® is a modified starch having a weight average molecular weight of 2,000; and Instant-n Oil® is a modified starch having a weight average molecular weight of 800,000; all are available from National Starch and Chemicals

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Corp., Bridgewater, NJ.

Superfloc® A-130 is a carboxylated polyacrylamide having a weight-average molecular weight of 12,000,000 to 14,000,000 and is available from Cytec Co., Stamford, CT.

5 Nonionic polyacrylamides PAM-a and PAM-b having a weight-average molecular weight of 15,000,000, and 5,000,000 to 6,000,000, respectively, are available from Scientific Polymer Products, Inc., Ontario, NY.

Polyethyleneimine having a weight-average molecular weight of 750,000 is available from Aldrich Chemical Co., Milwaukee, WI.

10 Parez® 631 NC is a low molecular weight glyoxylated polyacrylamide, and Parez® 802 is a low molecular weight glyoxylated urea resin, both are available from Cytec Co., Stamford, CT.

Pluronic® F87 is nonionic poloxomer, available from BASF corp., Parsippany, NJ.

15 Urea, sucrose and glyoxal (in 40% solution in water) are available from Aldrich Chemical Co., Milwaukee, WI.

#### EXAMPLE 6

A melt processable composition of the invention is prepared by mixing 45wt% starch (Crystal Gum), 40.5wt% urea, 4.5 wt% sucrose, and 9.8wt% free water, and manually stirring to form a slurry. Polyacrylamide (PAM-a, Mw = 15,000,000) is dissolved in water to form a PAM aqueous solution. An aliquot of the polymer/water solution is added to the slurry. Water in the slurry is then evaporated until the weight percent of polyacrylamide in the final mixture is 0.2wt%.

25 The composition has a shear viscosity of 0.65 Pa•s and an extensional viscosity of 1863.2 Pa•s, at 700s<sup>-1</sup> and 90°C.

#### COMPARATIVE EXAMPLE 6b

A comparative starch composition is prepared according to Example 6 except no polyacrylamide is added to the composition. The composition has a shear viscosity of 1.35 Pa•s and an extensional viscosity of 43.02 Pa•s, at 700s<sup>-1</sup> and 90°C. Example 6 and Comparative Example 6b demonstrate that addition of a small amount of high polymer decreases the shear viscosity slightly and significantly increases the

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extensional viscosity.

#### EXAMPLE 7

A melt processable composition of the invention is prepared by mixing 50wt% starch (Crystal Gum), 30wt% urea, 1.5 wt% sucrose, and 18.5wt% free water, and manually stirring to form a slurry. Polyacrylamide (Superfloc A-130, Mw = 12-14,000,000) is dissolved in water to form a PAM aqueous solution. An aliquot of the polymer/water solution is added to the slurry. Water in the slurry is then evaporated until the weight percent of polyacrylamide in the final mixture is 0.003wt%.

The composition has a shear viscosity of 1.12 Pa•s and an extensional viscosity of 46.0 Pa•s, at 700s<sup>-1</sup> and 90°C.

#### COMPARATIVE EXAMPLE 7b

A comparative starch composition is prepared according to Example 7 except no polyacrylamide is added to the composition. The composition has a shear viscosity of 1.23 Pa•s and an extensional viscosity of 0.69 Pa•s, at 700s<sup>-1</sup> and 90°C. Example 7 and Comparative Example 7b demonstrate that addition of a small amount of high polymer decreases the shear viscosity slightly and significantly increases the extensional viscosity.

#### EXAMPLE 8

A torque rheometer having a melt blowing die is used to process the composition of Example 6. The torque rheometer is illustrated in Figure 6. The torque rheometer assembly 100 includes a drive unit 110 (Model Rheocord 90 available from Haake GmbH), a barrel 120 partitioned into four temperature zones 122, 124, 126 and 128, a feed port 121, and a melt spinning die assembly 131. Twin screw elements 160 (model TW100, from Haake GmbH) are attached to the drive unit 110 and disposed within the barrel 120. A six inch wide melt blowing die assembly 131 (available from JM Laboratories, Dawsonville, GA) is connected to the end of the barrel via a pump 160. The die assembly has a spinneret plate which has 52 holes per linear inch and a hole diameter of 0.015" (0.0381cm), surrounded by a 0.02" wide air passageway 152, from which a high velocity air stream 151 impinges the extruded filaments just below the spinneret plate. The air stream has the effect of simultaneously blowing the filaments away from the spinneret and attenuating the filaments.

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The composition of is prepared (as described in Example 6) by mixing 45wt% starch (Crystal Gum), 0.2wt % polyacrylamide (PAM-a), 40.5wt% urea, 4.5 wt% sucrose, and 9.8wt% water. The mixture is gravity-fed via feed port 121 into a torque rheometer. The torque rheometer and die assembly are set as follows:

5	Barrel Temperature	
	Zone 122	70°C
	Zone 124	90°C
	Zone 126	90°C
	Zone 128	90°C
10	Torque	100 rpm
	Die Temperature	126.7°C
	Air Temperature	126.7°C
	Air Pressure	35 psi
	Pump	40 rpm

15 The mixture is conveyed from the extruder through the pump into the melt blowing die. The resulting attenuated filaments (or fine fibers) of the invention have fiber diameters ranging from 8 to 40 microns.

Note that the weight percent starch in the melt processable composition includes the weight of starch and the weight of bound water (which is on the average  
20 about 8 wt% of the starch). It is to be understood that the as-prepared compositions are used for uniaxial and biaxial extensional processes. However, most of the water is lost during the melt process, and the resulting starch fiber, film or like product contains little or no free water. The resulting product does contain some bound water (possible by absorbing moisture from ambient environment). Therefore, the composition of the  
25 resulting product may be more appropriately expressed by its solid components, calculated on a dry solid basis. For example, to calculate, on a dry solid basis, the composition of the fiber made according to Example 8, one would take out the 9.8 wt% free water from the overall composition and the 8wt% bound water from the starch, then normalize the remaining solid content to 100%. Thus, the composition of  
30 the fiber of Example 8 calculated on a dry solid basis would be 47.8 wt% starch solid (without bound water), 0.23 wt% polyacrylamide, 46.8 wt% urea and 5.2 wt% sucrose.

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EXAMPLE 9

The composition of Example 7 is melt blown into fine fibers of the invention. Figure 7a is the Scanning Electron Micrographs of fine starch fibers made from the composition of Example 7 using the process described in Example 8, shown on a 200 micron scale. Figure 7b is the Scanning Electron Micrographs of the same starch fibers shown on a 20 micron scale. Both figures show that starch fibers of Example 9 have a fairly consistent fiber diameter of about 5 microns.

EXAMPLE 10

Fifteen grams of starch (Crystal Gum, Mw=100,000 ) and fifteen grams of free water are mixed together at 80°C with manual stirring until the mixture becomes substantially homogeneous or gelatinizes. A high polymer (PAM-a, Mw=15,000,000) is dissolved in free water to form a PAM aqueous solution of known concentration. An aliquot of the polymer/water solution is added to the starch/water mixture such that the overall mixture contains 0.006 grams of PAM-a. Then the overall mixture is heated to evaporate water until the weight of the final mixture (starch, PAM-a and water) equals 30 grams. This mixture is subjectively shown to have suitable melt extensibility for drawing fibers.

EXAMPLES 11-13

Mixtures of starch (Crystal Gum), high polymer and water are prepared in the same manner as in Example 5. The final compositions of these mixture are shown below.

		Mw		Ex-11	Ex-12	Ex-138
Starch	Crystal Gum	100,000	wt%	49.99	49.99	46.92
Polyacrylamide	Superfloc A-130	12-14,000,000	wt%	0.02		
	PAM-b	5-6,000,000	wt%		0.02	
Polyethyleneimine		750,000	wt%			6.17
Water			wt%	49.99	49.99	46.91

These compositions of the invention are subjectively shown to have suitable melt extensibility for drawing fibers.

EXAMPLES 14-16

The following compositions are prepared in the same manner as Example 1.

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		Mw		Ex-14	Ex-15	Ex-16
5	Starch	Crystal	wt%	41.54	20.77	20.77
	Gum	100,000				
		Nadex	wt%		20.77	
		2,000				
		Instant-n	wt%			20.77
	Oil	800,000				
	Polyacrylamide	PAM-a	wt%	0.08	0.08	0.08
		15,000,00				
		0				
	Urea		wt%	6.23	6.23	6.23
	Sucrose		wt%	6.23	6.23	6.23
10	Parez 631 NC		wt%	1.04	1.04	1.04
	Water		wt%	44.88	44.88	44.88

These compositions of the invention are expected to have suitable melt extensibility for drawing fibers. And where the water has been adjusted to about pH 2, the resulting fibers are expected to have a water solubility of less than 30%, based on the test method disclosed herein.

#### EXAMPLE 17

A melt processable composition is prepared by mixing 45wt% starch (Crystal Gum), 0.2wt % polyacrylamide (PAM-a), 40.5wt% urea, 4.5 wt% sucrose, and 9.8wt% water to form a slurry. The composition is melt blown into fine fibers using a torque rheometer as shown in Figure 1c in the manner described in Example 8, except the mixture is meter-fed into the torque rheometer. The torque rheometer and die assembly are set as follows:

	Barrel Temperature	
25	Zone 122	70°C
	Zone 124	90°C
	Zone 126	90°C
	Zone 128	90°C
	Torque	140 rpm
30	Feed Rate	16 gm/min
	Die Temperature	137.8°C



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Air Temperature	137.8°C
Air Pressure	50 psi
Pump	40 rpm

The resulting attenuated filaments (or fine fibers) of the invention have  
5 fiber diameters ranging from 10 to 30 microns. The fibers are air laid onto a  
papermaking forming fabric as described in U.S. Patent No. 4,637,859, with the fabrics  
of U.S. Patent Nos. 5,857,498, 5,672,248, 5,211,815 and 5,098,519, all incorporated  
herein by reference, also being judged suitable for this purpose.

#### EXAMPLE 18

10 The resultant web from the air-laying process of Example 17 is tested  
for oil absorbency. A drop of a commercially available motor oil (SAE 20 grade, by  
the Society of Automobile Engineers' designation) is placed on the web and on a  
commercially available paper towel, respectively, for comparison of oil absorbency.  
The web shows an improved oil absorbency over that of the commercial paper towel in  
15 the following aspects: (1) the web absorbs oil faster than the commercial paper towel,  
as shown by a shorter residence time on the surface of the web; and (2) after 30  
seconds, the web has a spot size of about 1.5 to 2 times larger in diameter than that of  
the commercial paper towel.

#### EXAMPLE 19

20 This example illustrates that the starch composition of the present  
invention can be made into building materials, e.g., pressed board. A melt processable  
composition is prepared by mixing 60wt% starch (Crystal Gum), 0.1wt %  
polyacrylamide (SP2), 2wt% urea, 2 wt% sucrose, 1.5 wt% Parex 631 NC and 34.4  
wt% water (adjusted to pH 2 with sulfuric acid) to form a slurry. The slurry is fed in to  
25 a torque rheometer (Model Rheocord 90) as illustrated in Figure 1c and operated under  
the conditions as described in Example 17 above, except a single capillary die (having  
a 1 mm diameter and a temperature of 90°C) is used instead of a melt spinning die.  
The extruded strand is dusted with saw dust or wood shavings while still wet and  
sticky. The dusted strands are compressed together to form a log. The log is dried at  
30 40°C in a forced air oven for two hours to get rid of the residual water from the starch  
composition. The final product is a log of 47.8wt% saw dust and 52.2 wt% dried

starch composition.

#### EXAMPLE 20

This example illustrates that the present invention can be incorporated into structural materials as reinforcements. Though this example uses fibers made from a composition without high polymers. It is believed that when a composition of the present invention is used, the product would show better or equivalent performances.

A comparative cement sample is prepared as follows: 5 parts of commercially available Quikrete Anchoring cement are mixed with 1.5 part clean tap water until a thick syrup consistency is obtained. Within 5 minutes of mixing, the cement was introduced into cylindrical molds in order to obtain a constant dimension sample for evaluation. Thin wall molds 5" long and 0.23" in inner diameter (i.e., commercially available straws) are filled by driving the pasty cement mixture up from the bottom. This filling method eliminates air inclusion in the finished sample. The samples are allowed to cure for 5 days prior to evaluation. The mold is carefully scored on the outer surface so as not to damage the sample inside, then the mold is peeled away to retrieve the comparative sample (Example 20b).

A melt processable composition is prepared by mixing 45wt% starch (Durabond®, available from National Starch and Chemicals Corp., Bridgewater, NJ), 15 wt% urea, 15 wt% sorbitol, and 25 wt% water to form a slurry. The slurry is fed in to a torque rheometer (Model Rheocord 90) as illustrated in Figure 1c and operated under the condition as described in Example 19 above. The fibers are about 0.02" in diameter and are cut to 1" in length for use herein. The extruded, thin spaghetti-like strands are incorporated into cement as follows: 5 parts of commercially available Quikrete Anchoring cement are mixed with 1.5 part clean tap water and 0.5% (on a dry weight basis) starch fibers. The additional amount of water added herein is required to achieve the comparable consistency as the comparative sample above. The sample molds are filled and the samples (Example 20) are cured and retrieved in the same manner as above.

The samples are subjectively evaluated by bending to failure by hand. Example 20 are subjectively judged to be slightly weaker than the comparative Example 20b. Example 20 has an apparent density of 1.46g/linear inch while

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comparative Example 20b has an apparent density of 1.48g/linear inch. Therefore, it is demonstrated that Example 20 offers the benefits of light weight and lower cost (on a volume basis).

#### EXAMPLE 21

5                    This example illustrates that the composition of the present invention can prophetically be made into a controlled water release material when mixed with potting soil. The controlled water release is useful for horticultural and agricultural plants which thrive in a relatively low humidity environment and/or infrequent watering. A melt processable composition is prepared by mixing 50wt% starch  
10 (Durabond®, available from National Starch and Chemicals Corp., Bridgewater, NJ), 0.1wt % polyacrylamide (SP2®), 15 wt% urea, 15 wt% sorbitol, 1.5 wt% Parex® and 18.4 wt% water to form a slurry. The slurry is fed in to a torque rheometer (Model Rheocord 90) as illustrated in Figure 1c and operated under the condition as described in Example 19 above. The extruded, thin spaghetti-like strands are allowed to dry  
15 before mixing with potting soil. The ratio of starch-based strand to potting soil depends on the requirements of various types of plants. Generally, 10 wt% of starch-based strands in potting soil shows satisfactory water holding/release results.

                    Examples 22-24 use films made from compositions without the benefit of high polymers. It is believed that when a composition of the present invention is  
20 used in each of these examples, the resultant product would show beneficial improvements in properties, e.g., lower caliper, greater flexibility.

#### EXAMPLE 22

                    This example illustrates that the compositions of the invention can be made into thin films, using a Werner & Pfleiderer ZSK-30 co-rotating twin-screw  
25 extruder with a L/D ratio of 40. The screw configuration consists of four kneading sections and five conveying sections. The extruder barrel consisted of an unheated feed zone followed by seven heated zones, which are designated consecutively as Zones A, B, 1, 2, 3, 4 and 5. The barrel is controlled to the temperature profile summarized below, and the screw speed is set to 150 rpm.

30	Zone	A	B	1	2	3	4	5
	Temperature	50	50	50	95	95	95	95
	°C							

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## 15

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EXAMPLE 24

This example illustrates that the films of Example 22 are fusable such that the films can be made into substantially transparent bags/pouches useful as sealable food storage pouches, shopping bags, garbage bags, grocery bags, and the like. Two pieces  
5 of 4 inch by 4 inch (10.16cm by 10.16cm) films are overlaid with a piece of release paper interposed between them. The release paper should be smaller than the films so that at least three edges of the films are in direct contact with each other. A Vertrod impulse sealer (Model 24LAB-SP) is used to seal three sides of the overlaid films. The sealer is set at 50% voltage, 60 psi pressure, a six second dwell time (one second  
10 on and 5 seconds off), and for a total sealing time of one minute. The resultant bag shows uniform, welded seals on three sides. The fourth side can optional be sealed to form a completely sealed pouch.

EXAMPLE 25

This example illustrates the water-insoluble starch compositions of the present  
15 invention. A composition is prepared by mixing 50 wt% starch (Crystal Gum), a crosslinking additive (the type and the amount of the crosslinking additive are shown in the Table below) and a balance of water which has been adjusted to pH 2 using sulfuric acid. Where glyoxal (in 40% solution in water) is used, there is no need to adjust the water pH. The composition and test sample are prepared according to Test  
20 Method for Water Solubility described hereinabove. The results are shown in the Table below:

Solubility:

	<u>% Additive</u>	<u>Parez 631</u>	<u>Glyoxal</u>	<u>Parez 802</u>
	0.00%	37%	37%	37%
25	0.12%		16%	
	0.20%		10%	
	0.25%	28%		48%
	0.32%		11%	
	0.40%		7%	
30	0.50%	16%		16%
	0.75%	14%		9%
	1.00%	14%		6%
	1.50%	11%		4%

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The disclosures of all patents, patent applications (and any patents which issue thereon, as well as any corresponding published foreign patent applications), and publications mentioned throughout this description are hereby incorporated by reference herein. It is expressly not admitted, however, that any of the documents

5 incorporated by reference herein teach or disclose the present invention.

While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the spirit and scope of the invention. It is intended to cover in the appended claims all such changes and

10 modifications that are within the scope of the invention.

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CLAIMS

1. An absorbent, flexible structure comprising pseudo-thermoplastic starch fibers.
2. The structure of claim 1, wherein the starch fibers have a size ranging from about 0.01 dtex to about 135 dtex.
- 5 3. The structure of claim 1, wherein the structure has a geometric mean dry tensile strength ranging from about 10 g/cm to about 1200 g/cm, an initial geometric mean wet tensile strength ranging from about 2 g/cm to about 400 g/cm, and a geometric mean decayed wet tensile strength ranging from about 0 g/cm to about 20 g/cm.
4. The structure of claim 1, wherein the structure has a basis weight ranging from  
10 10 g/m<sup>2</sup> to about 450 g/m<sup>2</sup>.
5. The structure of claim 1, further comprising a plasticizer selected from the group consisting of sorbitol, monosaccharides, disaccharides, glycerol, polyvinyl alcohol, and polyethylene glycol, wherein said plasticizer comprises, based on total weight of the structure, from about 5 wt % to about 70 wt %.
- 15 6. The structure of claim 1, further comprising cross-linking agents selected from the group consisting of, polyamide-epichlorohydrin resins, urea-formaldehyde resins, glyoxylated polyacrylamide resins, melamine formaldehyde resins, polyethylenimine resins, Caldas 10 resin, CoBond 1000 resin, wherein said cross-linking agents are present in amounts ranging from about 0.1 wt % to about 10 wt. %, based on the total  
20 weight of the structure.
7. The structure of claim 1, wherein the structure has an absorbency ranging from about 1  $\frac{\text{g}_{\text{Water}}}{\text{g}_{\text{Dry Structure}}}$  to about 15  $\frac{\text{g}_{\text{Water}}}{\text{g}_{\text{Dry Structure}}}$ .
8. The structure of claim 1, wherein the structure has a total flexibility ranging from about 1.0 g/cm to about 75 g/cm.
- 25 9. A structure comprising pseudo-thermoplastic starch fibers wherein the fibers have a Tg of at least about -30 °C and the structure has a geometric mean decayed wet tensile strength ranging from about 0g/cm to about 20 g/cm and wherein said fibers have a size ranging from about 0.01 dtex to about 135 dtex.
10. An absorbent structure comprising one or more plies wherein at least one ply  
30 comprises pseudo-thermoplastic starch fibers, and wherein the at least one ply has a basis weight ranging from about 10 g/m<sup>2</sup> to about 100 g/m<sup>2</sup>, a GMDT ranging from

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about 40 g/cm to about 475 g/cm, an apparent density ranging from about 0.04 g/cm<sup>3</sup> to about 0.12 g/cm<sup>3</sup>, and an initial GMWT ranging from about 2 g/cm to about 200 g/cm.



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ABSTRACT

A flexible absorbent structure is produced comprising starch fibers. Naturally occurring starch in the presence of water, plasticizers and other additives is melt extruded and spun bonded to form low density, absorbent, flexible structures. The structures exhibit properties matching those of consumer paper products such as paper towels, toilet tissue, facial tissue, napkins, wet wipes, and the like.

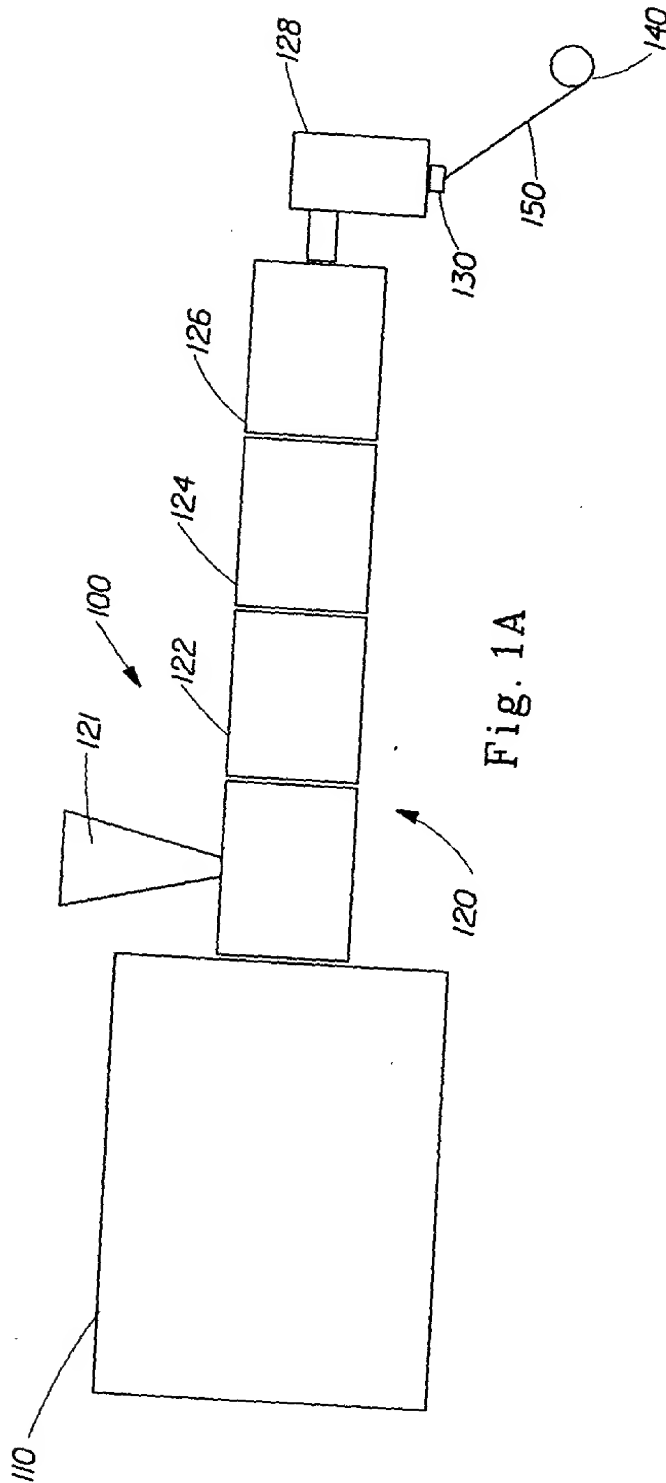


Fig. 1A

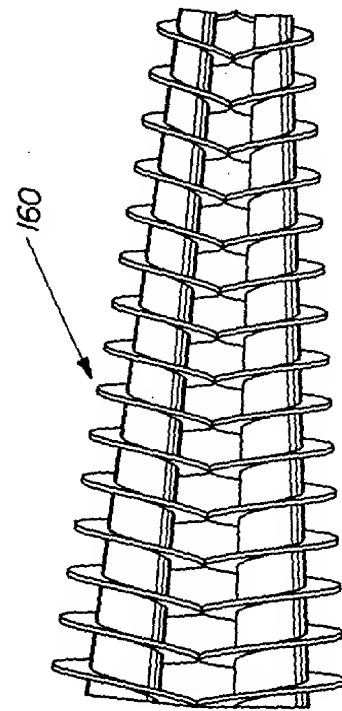


Fig. 1B

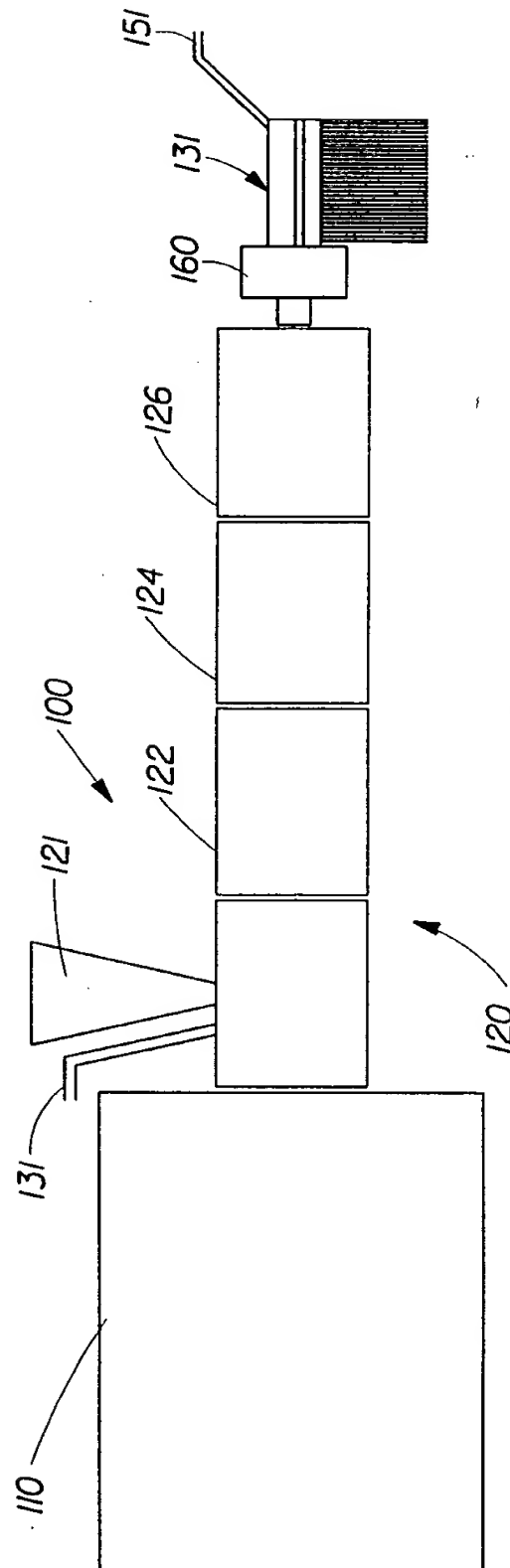


Fig. 1C

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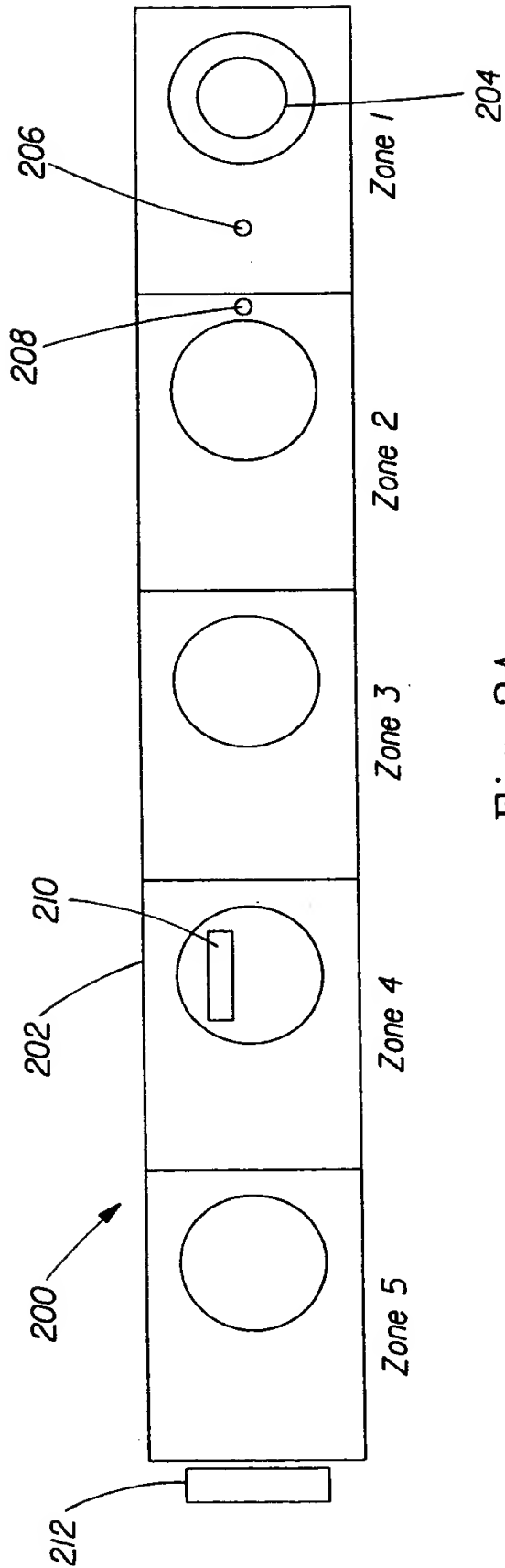


Fig. 2A

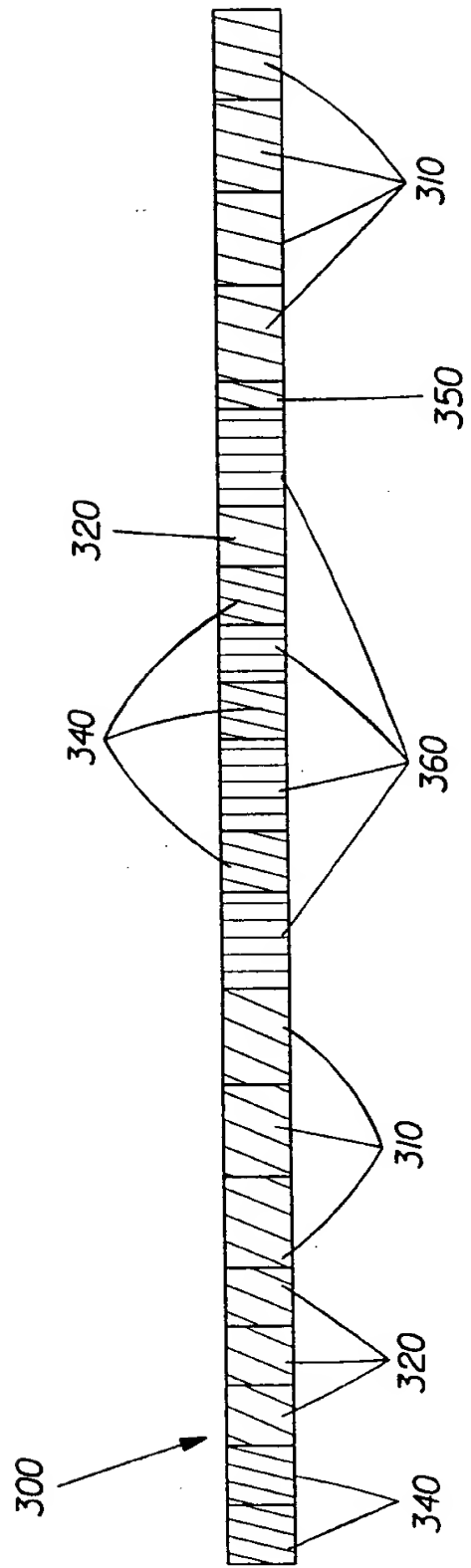


Fig. 2B

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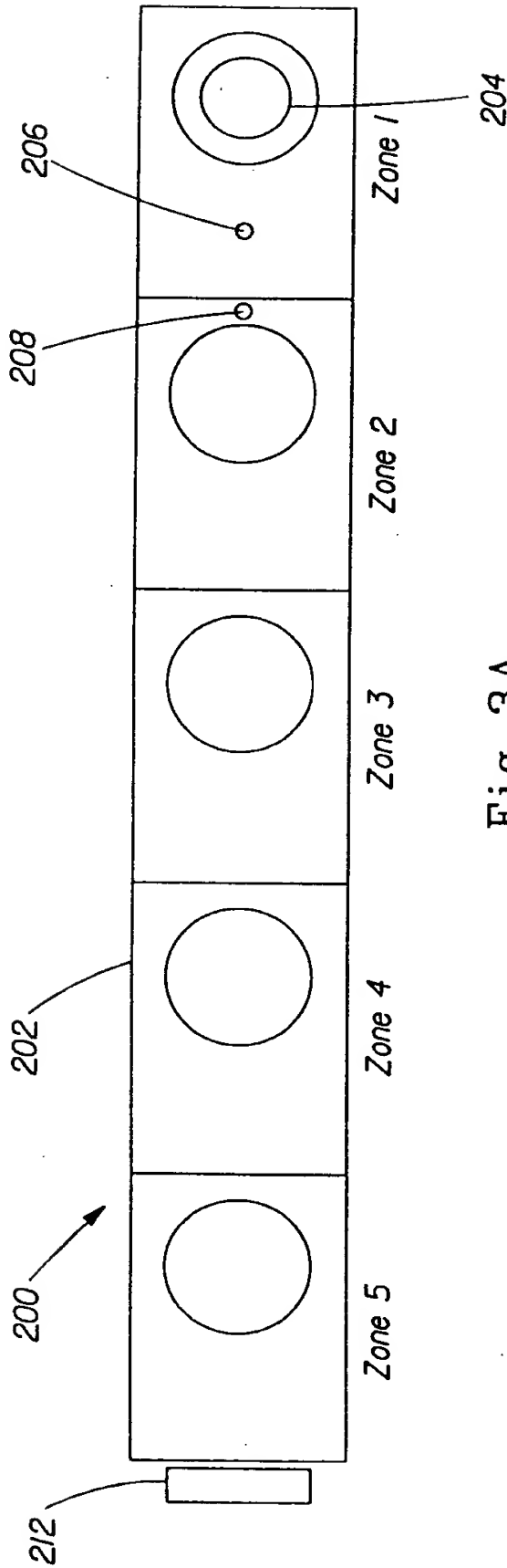


Fig. 3A

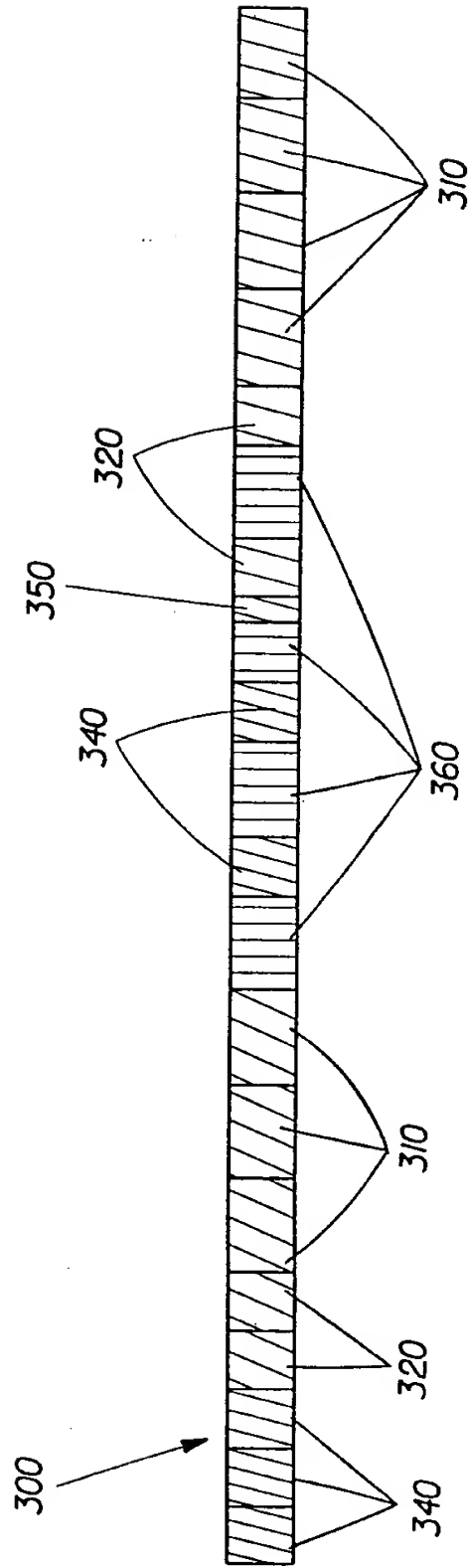


Fig. 3B

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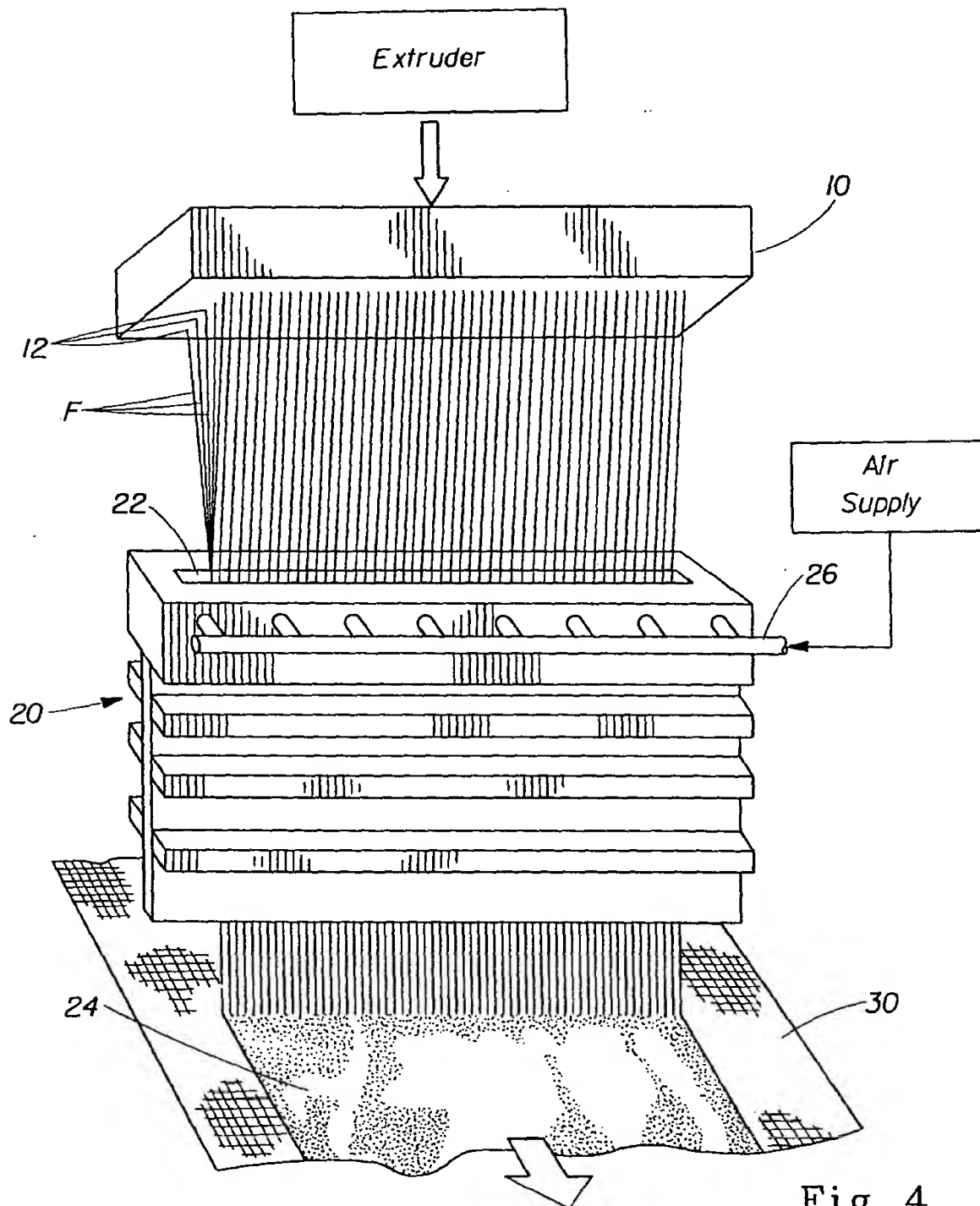


Fig. 4

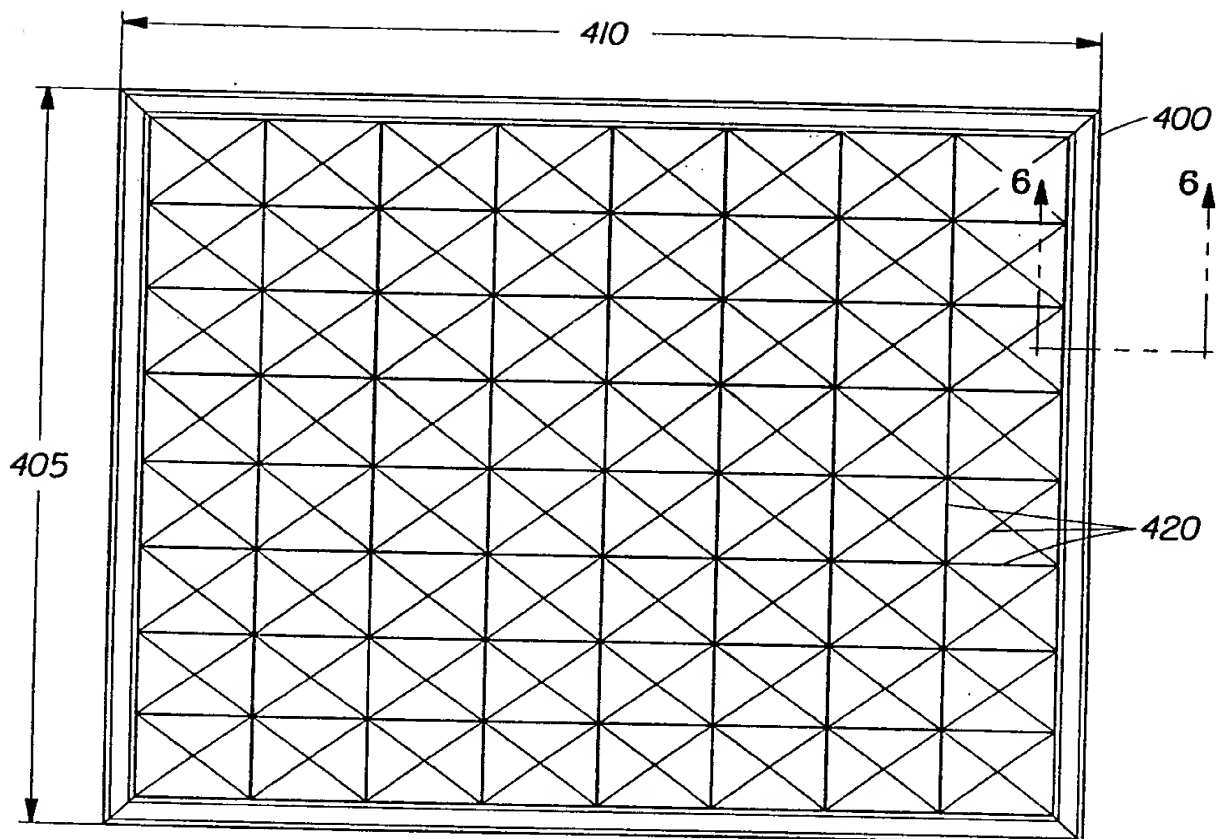


Fig. 5

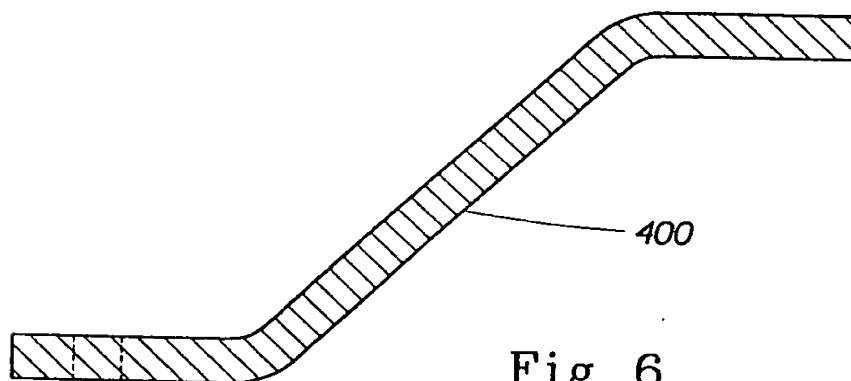


Fig. 6

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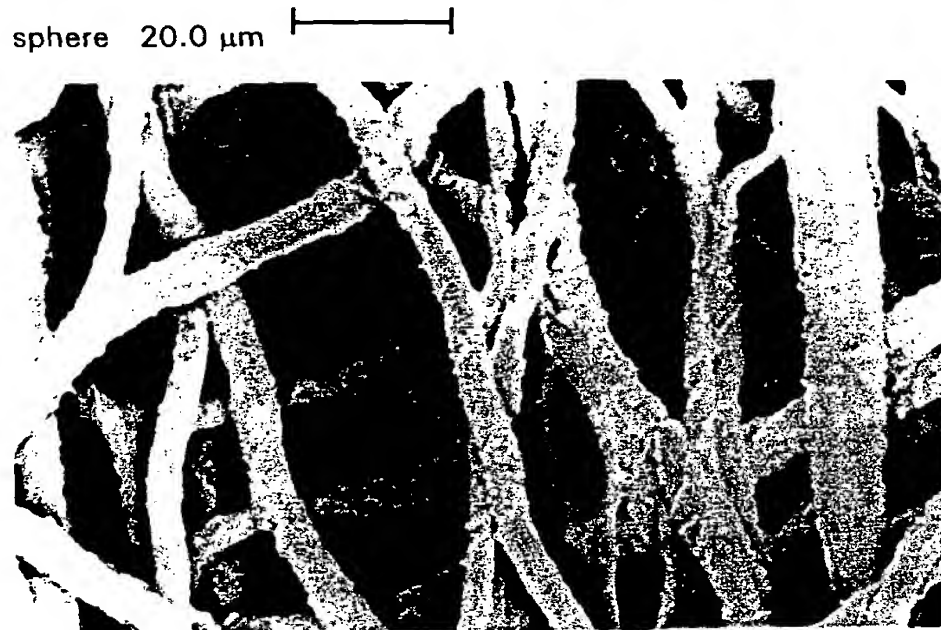


Fig. 7A

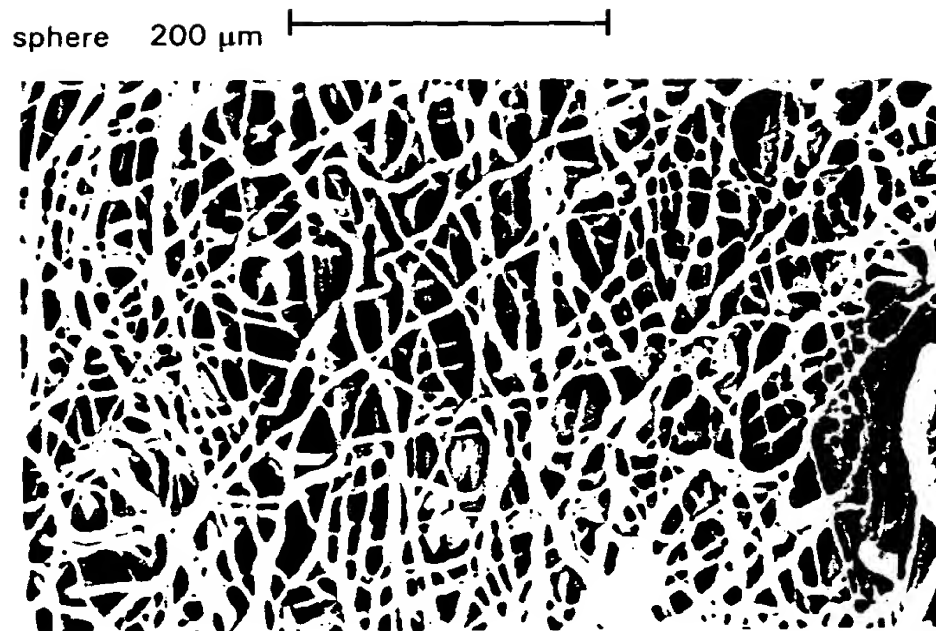


Fig. 7B